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SUPERCRITICAL GAS EXTRACTION OF NOVA SCOTIA COAL

FINAL REPORT

BY

RAYLO CHEMICALS LIMITED

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SUPERCRITICAL GAS EXTRACTION OF NOVA SCOTIA COAL

FINAL REPORT

DSS REFERENCE NO. 26 SQ.23440-2-9098

I. SUMMARY

Semi-continuous Extraction

Supercritical gas extraction of Nova Scotia high volatile bituminous coal carried out with various solvents revealed that 10% tetralin in toluene was the most efficient solvent. Extraction was effective in the range of 400 - 425°C but coking became greater as the temperature was increased. The yields of coal derived liquids (cdl) were higher at 2300 psig than at 1800 psig.

Continuous Extraction

Extraction of Forestburg subbituminous coal with toluene at 425°C and 3000 psig gave a cdl yield of 29.3% and the Nova Scotia high volatile bituminous coal yielded 31.5% of cdl under similar extraction conditions.

Analysis of Coal Derived Liquids

Coal derived liquids were fractionated by solvent analysis and the fractions analyzed by pmr and FT-IR spectroscopy. The oil content was very similar to that of the cdl from the Western Canadian Subbituminous coal. FT-IR analysis of cdl, char, and the original coal used showed the presence of some solvent derived materials in the coal derived liquids.

II. INTRODUCTION

The Energy Research Laboratories of CANMET awarded a contract to Raylo Chemicals Ltd. to investigate the supercritical gas extraction of Nova Scotia high volatile bituminous coal. The contract was issued by the Department of Supply and Services on November 4, 1982. The objectives of this program were:

1. To determine the suitability of Nova Scotia coal for liquefaction by supercritical gas extraction technique.
2. To ascertain the influence of a number of operating variables on the yield of coal derived products and to compare the results with the data obtained from the similar extractions of Forestburg subbituminous coal.
3. To convert the semi-continuous unit to continuous operation and to compare the extract yield with the yield obtained with the semi-continuous unit.

III. BACKGROUND

The technique of supercritical gas extraction first applied in the 1950's for deasphalting petroleum fractions has been extensively investigated by the British National Coal Board as a means for extracting thermally-generated non-distillable coal liquids at temperatures at which they undergo minimal repolymerization reactions. This method of separation which can be considered as a combination of

both extraction and distillation exploits the capability of a compressed supercritical gas to enhance the volatility of the organic compounds present in coal.

A schematic of the semi-continuous extraction apparatus is shown in Figure 1. Coal is mixed with liquid phase solvent and pressurized to the extraction pressure. On heating, the liquid phase solvent passes through its critical temperature and expands to form a gas phase solvent. At the extraction temperature, the coal is thermally depolymerized to form low molecular weight liquids, which are readily soluble in the gas phase, and a porous residue which contains virtually all the mineral matter associated with the coal. The solids remain in the autoclave and the gas phase is depressurized to precipitate the extract. Supercritical gas extraction offers a number of attractive features.

1. Readily available solvents which are liquids at ambient conditions can be used.
2. Separation of the extract from the solvent is easy and the recovered solvent can be reused.
3. The extract is essentially free of mineral matter and can be utilized for the preparation of substitute petroleum products.
4. The residual char is a suitable feedstock for gasification or combustion because of its high reactivity and freedom from coking.

The work described in this final report was originally reported in Raylo Progress Reports I through V covering the period from November 4, 1982 to March 31, 1983.

IV. EXTRACTIONS OF NOVA SCOTIA BITUMINOUS COAL

A. Description of Coal Samples

Two different samples of Nova Scotia high volatile bituminous coal were obtained from Cape Breton Development Corporation in 1982. The coals were crushed and comminuted to a particle size of 12 to -80 mesh (Table I). Table II shows the proximate analyses and calorific value of both coal samples and Table III the ultimate analyses. There were no significant differences between the basic analyses of the two coal samples. However, as compared to the Western Canadian subbituminous coal (1), Nova Scotia bituminous coal samples have lower moisture and ash contents, a larger fixed carbon content and a higher calorific value.

B. Semi-Continuous Extractions

1. Reaction Conditions

a) Procedures

The technique developed for the scg extractions of Western Canadian subbituminous coal (Method A) was found to cause severe coking of Nova Scotia bituminous coal. The coking was so severe that the method had to be modified (as Method B) to allow the extractions to be performed. The methods were:

METHOD A

A 300 grams sample of Nova Scotia bituminous coal was placed in the autoclave, the apparatus assembled and 350 ml of solvent was introduced by applying vacuum to the apparatus. The autoclave was heated to the desired temperature causing the pressure to rise. When the autoclave had reached the required pressure, solvent was pumped into the apparatus and the pressure was maintained by operating the pressure control valve. After the operating temperature was reached, an additional three litres of solvent was pumped through the system at a pumping rate of 22 to 28 ml/min. The time required to reach the operating temperature ranged from 140 to 157 minutes.

METHOD B

The procedure differed from Method A in that the solvent flow was started immediately after the start of the heating. After the operating temperature was reached, an additional three litres of solvent was pumped through the system. This modification increased the heat-up time and the total volume of solvent pumped was nearly twice the amount pumped in Method A. However, coking was reduced.

b) Extraction Solvents

Toluene was used as the reference solvent. Solutions of tetralin and toluene were used to test the effect of hydrogen donating mixture on the coal pyrolysis and extraction. Varsol with an aromatic content of about 20% was used as a representative of less costly, readily

available solvents. Mixtures of Varsol and toluene were tested to show the effect of increasing aromaticity and mixtures of Varsol, toluene and tetralin to show the combined effects of aromaticity and hydrogen donating power.

Other solvents were not tested for the supercritical gas extraction of Nova Scotia coal as previous studies had shown that most of these solvents were either unstable under the extraction conditions (e.g. p-cresol) or did not have sufficient solvent power to dissolve the coal derived liquids (e.g. n-heptane, n-decane).

c) Temperature and Pressure

The nominal extraction temperatures ranged from 375 to 425°C. These temperatures are nominal because some extract is withdrawn during the heat-up period and the amount so removed varies with the extraction method. In extractions by Method A, the release of gaseous material from the autoclave to prevent the pressure rising above the desired value removes some coal derived liquids from the system before the nominal temperature is realized. The extraction takes place over an even wider temperature range in extractions by Method B as solvent is passed through the system from the start of the heating. Figure 2, toluene extraction by Method B, shows that a significant fraction of the cdl is obtained at temperatures well below the nominal extraction temperature.

Extractions were carried out at pressures of 1800 or 2300 psig.

2. Results

a) Effect of Extraction Procedure and Solvent to Coal Ratio on Extract Yield of Nova Scotia Coal

Extraction by Method A results in a solvent to coal ratio of about 10:1 while extraction by Method B results in a ratio of about 20:1. The results of extractions with toluene (Table IV) and with 5% or 10% tetralin in toluene (Table VIII) by these two method show that cdl yields were higher and the amounts of char formed were lower in the extractions by Method B.

The effect cannot be ascribed solely to the difference in solvent to coal ratio because the extraction takes place over a wider temperature range in the extractions by Method B.

b) The Effect of Extraction Solvent

i) Toluene

Toluene (Tc = 321°C) is the reference solvent for supercritical gas extraction of coal. Extractions of samples 1 and 2 of the Nova Scotia bituminous coal (300 grams) were carried out over a range of temperatures and pressures.

Samples of the eluate were collected at regular intervals. The amount of water present in each fraction was determined by the Dean and Stark method. Solvent was removed from the samples under reduced pressure. The yields of cdl, the amount of water formed, and the char weight for each run are summarized in Table V.

Coal sample 1 gave a slightly higher yield of cdl than coal sample 2 under similar extraction conditions. Increasing the solvent to coal ratio from 9.5 to 17.6 and pressure from 2000 to 2300 psig led to substantially higher yield of coal derived liquids. In all cases, the char obtained was crusty and coke-like in appearance. As illustrated in Table V and Figure 2, the rate of extraction was low (17.3% of total cdl) in the temperature range of 25 - 200°C and maximum extraction took place between 325 - 400°C.

ii) 5 or 10% Tetralin in Toluene

A series of extractions were carried out with 5 and 10% tetralin in toluene (W/W) at different temperatures and pressures by extraction methods A & B. The yield of cdl was obtained by gc analysis of the mixture containing cdl, tetralin and naphthalene (tetralin dehydrogenation product), using n-decane as an internal standard (Table VI).

As observed in the extraction of Western Canadian subbituminous coal, addition of tetralin to toluene enhanced the coal pyrolysis reaction resulting in increased cdl yield and reduced char weight. The yield obtained with 10% tetralin in toluene was greater than the yield obtained with 5% tetralin in toluene. The char obtained was coke-like in appearance for all the extractions and coking increased as the content of tetralin in toluene was increased from 0 to 10%. Extractions carried out by Method B gave higher yield of cdl than were obtained by Method A.

iii) Varsol Based Solvent Mixtures

Varsol is an industrial solvent sold by Esso; the composition of which varies according to the refinery in which it is made. The Varsol used for these extractions had a boiling point range of 150 - 181°C and an aromatic content of 19%. Previous work had shown that Varsol is as good a medium as toluene for supercritical gas extraction of Western Canadian subbituminous coal (1).

In order to evaluate the effect of aromaticity and hydrogen donating capacity of the solvent on the extract yield, Nova Scotia bituminous coal sample 1 was extracted with Varsol at two levels of aromatic content (20 and 50%) and two levels of hydrogen donating capacity (0 and 10%) at 425°C and 2,300 psig. These extractions were carried out by Method B (Table VII). The higher material balances (100% or more) obtained for these extractions indicate the presence of some residual solvent in the coal derived liquids. It was difficult to remove the last traces of Varsol from cdl without losing at the same time some low boiling portion of the cdl. The char weight is, therefore, a better indicator of the degree of coal pyrolysis and extraction than is the yield of coal derived liquids.

Increasing the aromaticity of the solvent from 20 to 50% did not reduce the char weight. Similarly, addition of 10% tetralin to Varsol or to a mixture of Varsol and toluene did not have any significant effect on char weight. As compared to the toluene extractions carried

out under similar conditions, Varsol extractions gave a much higher char weight indicating that toluene is a better solvent than Varsol for supercritical gas extraction of Nova Scotia coal.

iv) Summary of Solvent Effects

As is evident from Table IX and Figure 3, among the four solvent systems investigated, 10% tetralin in toluene gave the highest yield of cdl and lowest char weight.

The char obtained was coke-like in appearance in all the four extractions. The extent of coking was somewhat lower when toluene and Varsol were used as the solvent and increased as the content of tetralin was increased in the solvent system. The Nova Scotia coals behaved differently from the Western Canadian subbituminous coal which showed no signs of coking under similar conditions.

c) The Effects of Temperature and Pressure

i) Temperature

It is well established that effective coal pyrolysis reaction occurs when coal is heated above 400°C. At temperatures above about 425°C the thermal degradation of the solvent becomes the limiting factor.

Extractions were carried out in the temperature range of 375 - 425°C and 1800 psig using Method B and the results are summarized in Table X and Figure 4.

The yields of coal derived liquids were higher and char weights were lower at 425°C than at 375°C.

ii) Pressure

Extractions of Nova Scotia coal were compared at a pressure of 1800 and 2300 psig. These extractions were carried out according to Method B using 5 and 10% tetralin at 375°C (Table XI and Figure 5). Extractions carried out at 2300 psig led to a higher yield of cdl and lower char weight. Thus a pressure of 2300 psig appears to be preferable for the supercritical gas extraction of Nova Scotia coal.

3. Overview and Conclusions

Comparison of the yields of cdl obtained using different solvents is difficult because the cdl obtained by Varsol based solvents are contaminated with the higher boiling fractions of Varsol and the cdl obtained by tetralin containing solvents contain tetralin and naphthalene which have to be estimated by gc. The relative weights of char are therefore particularly useful for comparisons of the extent of extraction between extractions by different solvents. A total of 20 supercritical gas extractions of Nova Scotia bituminous coal samples 1 and 2 were carried out using the semi-continuous extraction apparatus. The char weights, which reflect the degree of coal pyrolysis and extraction efficiency, are summarized in Table XII.

Both samples of Nova Scotia bituminous coal coked severely during the extractions. This coking, more than any property, would seem to limit the use of these coals as feedstocks for supercritical gas extraction. Coking was at its lowest when toluene or Varsol were used

as the solvent but became severe as the content of tetralin was increased from 0 to 10%. Similarly increasing the temperature of extraction from 375°C to 425°C led to increased coking.

B. Continuous Extractions

1. Technique

Semi-continuous extraction has been a useful and convenient exploratory method but is unsuitable for the control of some important variables. Further investigation of the process required a change to fully continuous extraction in which a slurry of coal in the solvent would be pumped through a reactor, the char separated and the cdl collected by reducing the pressure of the gas phase solution.

The continuous reactor was expected to give rapid heat-up to and close control of the reaction temperature. The unit would also allow the effects of the solvent to coal ratio and the residence time to be studied. The limited funds and time available would restrict the study to a demonstration that continuous flow operation is possible and a few exploratory runs.

2. Apparatus

A tubular, plug flow, reactor was chosen for these trials. Except for a high pressure char separator which had to be purchased, the continuous extractor was constructed from components previously used in the semi-continuous extraction study. A schematic diagram of the assembled apparatus is shown in Figure 6.

a) Slurry Feed

The slurry feed vessel contains a suspension of -100 mesh coal in the desired amount of solvent. The slurry is circulated by a centrifugal pump, past the inlet of the high pressure pump. This assures a uniform slurry and positive pressure feed to the high pressure piston metering pump which supplies a set flow through the tubular plug-flow reactor.

b) Tubular Reactor

The tubular plug-flow reactor consists of 17 feet of 1/4 inch O.D. x 0.035 in. wall 316 stainless steel tubing formed into a 10 inch diameter 8 turn helical coil having a working pressure of 5315 psig at 427°C and a total volume of 85 ml (4.48 ml/ft.). The coil surrounds the char separator.

c) Char Separator

The separator is an inverted high pressure autoclave manufactured by High Pressure Equipment Co. of Erie, Pennsylvania. The separator is 10 inches long, 2.5 inches in O.D., has a capacity of 280 ml and a working pressure of 7000 psig at 343°C. The reaction products from the tubular reactor are fed into the bottom of the separator through a quarter inch 316 stainless steel tube which extends close to the top where it directs the char downward by virtue of a 180° bend and the gaseous extracts leave through the filter at the top (Figure 7).

d) Temperature Control

The reactor and char separator were immersed in a fluidized sand bath which allowed the temperature to be controlled to within 2°C. The fluidized sand bath was mounted on a hydraulic hoist to allow the equipment to be set-up and leak tested before immersion in the bath.

e) Pressure Control and Recovery of cdl

A high pressure needle valve, Valve #1 in Figure 6, was controlled manually to maintain the system pressure constant at a pressure up to 5000 psig. The pressure was let down to atmospheric by this valve and the cdl and the bulk of the solvent collected in a stainless steel vessel (Item #10 in Figure 6). The remaining solvent vapours were condensed in a glass condenser and collected in a glass flask (Items #12 and 13 in Figure 6).

3. Commissioning

Initially, a blank run was carried out with toluene to test the apparatus for valve, pump, or connection failures. The tubular reactor and char receiver were immersed in the sand bath and purged with nitrogen at room temperature. The apparatus was filled with toluene by applying vacuum at the gas vent on the system. The toluene from the supply vessel was recirculated by the IWAKI centrifugal pump which also supplies a moderate pressure to the high pressure metering pump through a half inch stainless steel tee. The sand bath was heated up to 400°C. At a temperature of 400°C and 3000 psig, solvent leakage was observed

at various points in the system. After disassembly, the mating surfaces of the leaking joints were lapped and polished. The compression seals and rings of the pump valves also required fine grinding and lapping before the pump could deliver the solvent volume specified by the manufacturer. These modifications eliminated the leakage and allowed the pressure to be taken as high as 4000 psig.

4. Extraction Procedure

The apparatus was purged with nitrogen at room temperature and filled with toluene using vacuum. The tubular reactor and char catch-pot were immersed in the fluidized bath and heated to the operating temperature. The pressure was allowed to rise to the desired value and maintained there by opening the pressure control valve slightly as required. The slurry prepared from -100 mesh coal was kept suspended in the supply vessel using an IWAKI centrifugal pump. When the apparatus had reached the desired temperature, the high pressure pump was started to begin the extraction. Coal slurry was pumped through the system at constant temperature and pressure.

The extraction was terminated by stopping the high pressure pump and by closing the ball valve immediately ahead of the pump. The pressure controlling valve was slowly opened to allow reactor pressure to drop to about 250 psig. The sand bath was then lowered, control valve fully opened and the reactor was purged with nitrogen.

5. Extractions

The Nova Scotia bituminous coal samples had shown a strong tendency towards coke formation in the semi-continuous extractions. It was decided, therefore, to test the continuous extraction using the non-coking Western Canadian subbituminous coal to reduce the risk of blockages.

Three supercritical toluene extractions of Forestburg subbituminous coal and one extraction of Nova Scotia bituminous coal was carried out at 425°C and 3000 psig using different solvent to coal ratios. The results of these experiments are summarized in Table XIII.

6. Observations

a) Reaction Conditions

i) Temperature and Pressure

A temperature of 425°C was chosen based on the results of semi-continuous extraction. The temperature could be varied readily, if required. A pressure of 3000 psig was used in all the runs. This pressure is higher than used in most of the semi-continuous runs but the feed pump worked more reliably with a substantial back pressure.

ii) Solvent to Coal Ratio

The solvent to coal ratio for the extractions carried out was varied from 7.2 to 12.4. This ratio was limited by high pressure feed pump. Attempts to decrease the solvent to coal ratio resulted in coal forming a plug at the inlet valve.

iii) Residence Time

A residence time in the tubular reactor of 6 to 7 minutes was used. The limited time available did not allow variations to be tried.

iv) Equipment Limitations

The high pressure feed pump was the limiting unit in the apparatus. This is not surprising as the pump was a standard liquid feed pump and was being asked to pump a slurry. With some modification to the inlet and outlet valves the pump reliability could be improved.

b) Extraction Results

i) Production of Extract

The rates of water and cdl formation both remained constant throughout the extraction run, showing that the extraction was behaving as expected.

ii) Yield

In extraction of Forestburg subbituminous coal the yield ranged from 17.3 to 29.3% on a dry coal basis. The yields of cdl, although quite variable, are in a range similar to those obtained with the semi-continuous extraction apparatus. The yield of cdl from the Nova Scotia bituminous coal at 31.5% was slightly better than had been obtained in semi-continuous extractions.

iii) Coking

The Western Canadian subbituminous coal remained non-coking. Coking of Nova Scotia bituminous coal was not as severe a problem in the continuous extraction as it had been in the semi-continuous unit.

7. Conclusion

The feasibility of using a simple plug-flow reactor for continuous supercritical gas extraction of coal was successfully demonstrated. The results of this preliminary study of continuous extractions were sufficiently encouraging to suggest that, if further study of this coal liquefaction process is warranted, the work should be done on a fully continuous unit.

V. SOLVENT ANALYSIS OF COAL DERIVED LIQUIDS

Solvent analysis is a standard procedure employed for the separation and characterization of coal derived liquids. The separation scheme divides the mixture into four main groups:

1. Insoluble (THF insoluble).
2. Preasphaltene (THF soluble toluene insoluble).
3. Asphaltene (toluene soluble pentane insoluble).
4. Oil (pentane soluble).

The procedure followed was essentially the literature procedure (2,3,4). The asphaltenes were further fractionated into acid-neutral and basic fractions. The flow diagram of the procedure is presented in Figure 8.

A. Samples

Separate samples of the total cdl obtained by toluene extraction of Nova Scotia bituminous coal (sample 1 and 2) were prepared for solvent analysis.

B. Separation Procedure

1. Toluene Soluble and Insoluble Fractions

The bulk sample was liquefied by heating to 100°C and a 10 g analytical sample weighed out. The sample was slurried with toluene (100 ml) at 100°, filtered through a tared Soxhlet thimble and extracted with toluene (300 ml) for 24 hours. The thimble and contents, toluene insoluble fraction, were dried at 80° under vacuum to constant weight. The combined toluene solutions were concentrated on a rotary evaporator and then dried at 80°C in a vacuum oven to constant weight to leave the toluene soluble fraction.

2. Preasphaltene and THF Insoluble Fractions

The thimble containing the toluene insoluble material was extracted with 300 ml of THF for 24 hours. The thimble was dried to give the weight of THF insoluble material. The THF extract was concentrated on a rotary evaporator and then dried to obtain the weight of preasphaltene.

3. Oil and Asphaltene Fractions

The toluene soluble material was redissolved in toluene (3 ml of toluene per gram of toluene soluble material) on a steambath and diluted with pentane (2.0 ml of pentane per ml of toluene). The precipitate was collected by filtration through a tared (previously dried at 100°C) thimble and extracted with 300 ml of pentane in a Soxhlet extraction apparatus for 24 hours. The thimble was dried to

give the weight of asphaltene. The combined pentane solution was concentrated on a rotary evaporator and dried to obtain the weight of oil.

4. Acid-Neutral and Basic Fractions of Asphaltene

The thimble containing the asphaltene was extracted with 200 ml of toluene for 24 hours. The thimble was dried to obtain the weight of insoluble material. The toluene solution containing the soluble asphaltene was treated with HCl gas for 2 hours. The precipitated salts were collected by filtration, stirred with 200 ml of 0.3N NaOH for 2 hours and extracted with toluene (3 x 150 ml). The toluene solution was concentrated and dried to obtain the weight of basic asphaltene.

The toluene filtrate containing acid-neutral material was concentrated and dried.

C. Composition

The results of the fractionation of the samples of cdl obtained by semi-continuous toluene extraction of Nova Scotia coal samples 1 and 2 are given in Table XIV. The proportions of asphaltenes and oils in the samples were slightly different:

	Asphaltene %	Oil %
Sample 1	32.1	46.9
Sample 2	28.3	52.7

The average oil content was very similar to the oil content (52.1%) of cdl from Western Canadian subbituminous coal.

The further separation of the asphaltene fractions of the Nova Scotia cdl samples (Table XV) showed that the asphaltene compositions were also slightly different:

	Acid-Neutral %	Basic %
Sample 1	36.1	31.7
Sample 2	40.6	21.9

VI. NMR ANALYSIS OF COAL DERIVED LIQUIDS

A. Method

Proton nmr spectra were used to estimate the ratio (Ha) of aromatic and phenolic hydrogens to the total hydrogen. The spectra were recorded in $CDCl_3$ or pyridine-d_5 using a Varian T-60 spectrometer. Chemical shifts are relative to tetramethylsilane used as an internal standard.

B. Variation With the Extent of Extraction of the Aromaticity of the cdl Produced in a Semi-Continuous Extraction

Samples were collected during an extraction initially with every 25°C increase in temperature after the required pressure (2000 psig) was reached, and then every 15 minutes after attaining the operating temperature (400°C). Each fraction was concentrated and then analyzed by pmr spectroscopy.

The amount of aromatic matter increases in the latter stages of the extraction (Table XVI). Substantial amounts of bibenzyl was formed in the temperature range of 375 - 400°C (fractions 3 to 12).

C. Aromaticity of Fractions of cdl Obtained by Solvent Analysis

The values of Ha formed for the various fractions of cdl are not very consistent (Table XVII) but the preasphaltene, the acid-neutral asphaltene and the basic asphaltene fractions are more aromatic than the oil fractions. The pmr spectra of the cdl fractions obtained for Nova Scotia coal sample 2 are reproduced in Figures 9 to 12.

VII. FT-IR ANALYSIS OF COAL, COAL DERIVED LIQUIDS AND CHAR

A. Method

FT-IR spectra of the solid samples were obtained by KBr discs and of the liquid samples by THF casts using a Nicolet spectrometer.

Band assignment for the FT-IR spectrum of oil is summarized in Table XVIII. The FT-IR spectra for various samples are reproduced in Figures 13 to 19.

B. Coal Derived Liquid Fractions

1. Oil

The spectrum displays bands at 3525 cm^{-1} and 3380 cm^{-1} associated with hydrogen bonded phenolic OH or NH stretch, a sharp band at 3015 cm^{-1} arising from aromatic C-H stretch, and three bands at 2945, 2915 and 2842 cm^{-1} associated with C-H stretching. The band at 1600 cm^{-1} can be assigned to aromatic ring resonance enhanced by OH substitution. A strong band at 1447 cm^{-1} is associated with CH_2 bending mode and a band at 1375 cm^{-1} is due to CH_3 groups. A series of absorptions at 1255, 1190, 1150, 1080 and 1027 cm^{-1}

are generally associated with CH_2 rocking when several CH_2 groups are linked together. The presence of bands at 700 and 747 cm^{-1} is a strong indication of benzyl substituted structures.

2. Acid-Neutral and Basic Asphaltene

The spectra of acid-neutral and basic asphaltenes are very similar. A band at 1700 cm^{-1} in the spectrum of acid-neutral asphaltene is associated with carbonyl group of ketones, aldehydes and carboxylic acids. The spectrum of basic asphaltene shows only trace absorption at 1700 cm^{-1}. The bands at 3340, 1255 and 800 cm^{-1} in the spectrum of the acid-neutral asphaltene are significantly stronger than their counterparts in the spectrum of basic asphaltene.

3. Preasphaltene

Spectrum of preasphaltene is very similar to the spectra of acid-neutral and basic asphaltene showing only a difference in the relative intensity of absorption bands. The bands at 2960, 1600, 1430 and 700 cm^{-1} are weaker and bands at 1015 and 800 cm^{-1} are stronger than their counterparts in the spectrum of basic and acid-neutral asphaltene.

4. THF Insoluble Material

Spectrum of THF insolubles displayed absorption bands similar to those in the spectrum of preasphaltenes but the relative intensities were different. In contrast to the spectrum of preasphaltene, the spectrum of THF insolubles had a strong band at 1600 cm^{-1} due to aromatic ring stretching and relatively weak absorptions at 1260 and 800 cm^{-1}.

C. Comparison of Coal and Char

The FT-IR spectra of Nova Scotia coal and char are compared in Figure 18. The bands at 2915, 2842 (aliphatic C-H stretching), 1600 (aromatic ring containing phenolic oxygen), and 1439 cm^{-1} (CH_2 bending) in the spectrum of char are weaker than their counterparts in the spectrum of coal. This change corresponds to a loss of hydrogen rich materials from the coal and is confirmed by the ultimate analysis of the char. A sharp band at 700 cm^{-1} attributed to solvent derived benzyl type structures is not present in the spectrum of the char indicating that incorporation of solvent derived materials in the char is minimal.

D. Comparison of Coal and cdl

The FT-IR spectra of coal and cdl are presented in Figure 19. The significant difference between the two spectra is the presence of a new absorption band at 700 cm^{-1} in the spectrum of cdl. This absorption arising from benzyl type structures was also observed in all the fractions of solvent analyzed cdl. The formation of bibenzyl in the supercritical toluene extraction of coal is well documented in the literature (5) and has been observed by us in previous work with Western Canadian subbituminous coal.

E. Conclusions

FT-IR spectroscopy is a powerful analytical tool for the qualitative identification of functional groups associated with each fraction of cdl and is useful for the detection of solvent derived materials in coal derived liquids.

VIII. PROXIMATE AND ULTIMATE ANALYSIS OF CHARS

Proximate and ultimate analysis of chars obtained by supercritical toluene extraction of both Nova Scotia coal samples are summarized in Tables XIX and XX.

There is no significant difference in the calorific value of chars and the original coals used for the extraction. As expected, the volatile matter in the char was considerably lower and the fixed carbon content higher than in the original coal. Ultimate analysis of char shows a large decrease in hydrogen, oxygen and sulfur content, and an increase in carbon content from the amounts present in the coal. The ratio of hydrogen to carbon is 0.54 for char and 0.78 for the coal used for the extraction.

IX. REFERENCES

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2. M.J. Mima, H. Schultz and W.E. McKinsty, "Analytical Methods for Coal and Coal Products", C. Karr, Jr., Ed., Vol. 1, p. 557 (1978).
3. F.W. Steffgen, K.T. Schroeder and B.C. Bockrath, Anal. Chem., 51, 1164 (1979).
4. B.C. Bockrath, C.L. Delle Donne and F.K. Schweighardt, Fuel, 57, 4 (1978).

5. Chemical Nature of the Oil Formed by Hydrogenation, Supercritical Gas Extraction and Soxhlet Extraction of the Same Oil, John R. Kershaw, S. Afr. J. Chem., 30, 205 (1977).

TABLE I

Size analysis of Nova Scotia bituminous coal used for semi-continuous supercritical gas extraction experiments.

Sample [a]	Particle Size (mesh)	% of Total
1 [b]	+12	0.8
	-12 +24	17.7
	-24 +80	57.5
	-80	24.0
2	+12	4.2
	-12 +24	26.9
	-24 +80	52.6
	-80	16.3

a) Supplied by Cape Breton Development Corporation.

b) Metallurgical Coal (Sample dried at 60°C and 3mm to facilitate sieving).

TABLE II

Proximate analysis and calorific value of Nova Scotia high volatile bituminous coal.

Sample [a]	Determined	Moisture	Ash	Volatile Matter	Fixed Carbon	Btu/lb
1	As Received	8.2	2.9	31.9	57.0	13703
	Dry Basis		3.2	34.7	62.1	14928
2	As Received	7.8	3.5	31.8	56.9	13048
	Dry Basis		3.8	34.5	61.7	14147

a) Supplied by Cape Breton Development Corporation.

TABLE III

Ultimate analysis of Nova Scotia high volatile bituminous coal.

Sample [a]	Determined	C	H	N	S	O	H/C
1	As Received	76.13	4.96	1.55	1.15	5.04	
	Dry Basis	82.93	5.40	1.69	1.25	5.49	
	daf	85.70	5.58	1.74	1.29	5.67	0.78
2	As Received	72.96	4.66	1.34	2.18	7.64	
	Dry Basis	79.10	5.05	1.45	2.36	8.29	
	daf	82.18	5.25	1.51	2.46	8.61	0.77

a) Supplied by Cape Breton Development Corporation.

TABLE IV

Semi-continuous supercritical toluene extraction of 300 grams of Nova Scotia coal under various experimental conditions.

Sample	Method	Solvent/ Coal Ratio (W/W)	Temp. (°C)	Pressure (psig)	cdl (g)	Char (g)	% cdl (daf)	Material Balance [a]
2	A	10.4	400	2000	41.8	214.6	15.9	94.8
2	B	14.2	400	2000	41.4	208.3	15.8	92.6
1	A	9.5	400	2000	48.6	204.9	18.6	93.8
1	B	17.6	375	2300	71.6	195.9	27.4	98.5

a) Includes 28 grams water.

TABLE V

Extraction rate (grams of cdl per 1000 grams of toluene) at various temperatures in the semi-continuous supercritical toluene extraction of Nova Scotia bituminous coal sample 2 at 2000 psig.

Fraction	Temp. (°C)	Water (g)	cdl (g)	Toluene (g)	g cdl/1000 g toluene
1	25 - 40	--	0.20	397.1	0.50
2	40 - 85	1.00	0.39	327.0	1.19
3	85 - 127	1.25	1.52	280.3	5.42
4	127 - 174	1.75	3.02	327.0	9.24
5	174 - 210	1.50	4.45	327.0	13.61
6	210 - 264	4.00	5.06	350.4	14.44
7	264 - 300	2.75	3.73	210.2	17.75
8	300 - 325	2.50	7.02	327.0	21.44
9	325 - 350	0.25	2.31	116.8	19.78
10	350 - 375	trace	3.73	233.6	15.97
11	375 - 400	trace	3.68	256.9	14.32
12	400 - 420	--	4.74	350.4	13.53
13	420 - 420	--	3.45	350.4	9.85
14	420 - 405	--	2.08	350.4	5.94
15	405 - 400	--	1.66	350.4	4.74
16	400 - 397	--	1.59	350.4	4.54
17	397 - 394	--	1.45	350.4	4.14
18	394 - 394	--	1.56	420.5	3.71
Washings from catch pot and solvent receiver			3.56		

TABLE VI

Semi-continuous supercritical gas extraction of 300 grams of Nova Scotia coal sample 1 with different levels of tetralin in toluene under various experimental conditions.

Extraction Method	% Tetralin	Solvent/ Coal Ratio (W/W)	Temp. (°C)	Pressure (psig)	cdl (g)	Char (g)	% cdl (daf)	Material Balance [a]
A	3	9.8	300-375[b]	2000	30.1	228.5	11.5	95.5
B	5	26.5	375	1800	--	196.1	--	--
B	5	16.1	375	2300	59.4	184.9	22.7	90.8
B	5	24.4	400	1800	63.7	192.3	24.4	94.7
B	5	22.1	425	1800	70.2	171.5	26.8	89.9
A	5	14.2	425	1800	50.0	202.2	19.1	93.4
B	10	24.6	375	1800	73.0	180.0	27.9	93.7
B	10	22.7	375	2300	76.9	166.1	29.4	90.3
A	10	11.6	425	2300	34.7	208.2	13.3	90.3
A	0	9.5	400	2000	48.6	204.9	18.6	93.8

a) Includes 28 grams water.

b) Wide fluctuation in temperature of the autoclave was observed.

TABLE VII

Effects of aromaticity and hydrogen donating capacity of the solvent on extract yield in the semi-continuous supercritical gas extraction of Nova Scotia coal sample 1 at 2300 psig.

Solvent	Solvent/Coal Ratio (W/W)	Temp. (°C)	cdl (g)	Char (g)	% cdl (daf)	Material Balance [a]
Varsol [b]	16.5	400	59.6	212.4	22.8	100.0
Varsol [b]	22.9	425	68.0	211.5	26.0	102.5
30% Toluene in Varsol [c]	21.3	425	60.8	217.1	23.3	101.9
10% Tetralin in Varsol	22.7	415	d)	217.5	--	--
Varsol + Toluene + Tetralin (6:3:1)	21.1	375	d)	216.6	--	--

a) Includes 28 grams water.

b) 20% aromatic content.

c) 50% aromatic content.

d) Could not be determined accurately by gc due to the presence of residual Varsol in cdl.

TABLE VIII

Effect of extraction procedure and solvent to coal ratio on extract yield in the semi-continuous supercritical gas extraction of 300 grams of Nova Scotia coal sample 1.

Extraction Method	Solvent	Solvent/ Coal Ratio (W/W)	Temp. (°C)	Pressure (psig)	cdl (g)	Char (g)	% cdl (daf)	Material Balance [a]
A	Toluene[b]	10.4	400	2000	41.8	214.6	15.9	94.8
B	Toluene[b]	14.2	400	2000	41.4	208.3	15.8	92.6
A	5% Tetralin in Toluene	14.2	425	1800	50.0	202.2	19.1	93.4
B	5% Tetralin in Toluene	22.1	425	1800	70.2	171.5	26.8	89.9
A	10% Tetralin in Toluene	11.6	425	2300	34.7	208.2	13.3	90.3
B	10% Tetralin in Toluene	22.7	375	2300	76.9	166.1	29.4	90.3

a) Includes 28 grams water.

b) Coal sample 2 was used for these extractions.

TABLE IX

Effect of solvent on extract yield of semi-continuous supercritical gas extraction of 300 grams Nova Scotia coal sample 1 at 375°C and 2300 psig.

Solvent	cdl (g)	Char (g)	% cdl (daf)	Material Balance [a]
Toluene	71.6	195.9	27.4	98.5
5% Tetralin in Toluene	59.4[b]	184.9	22.7	90.8
10% Tetralin in Toluene	76.9[b]	166.1	29.4	90.3
Varsol[c]	59.6	212.4	22.8	100.0

a) Includes 28 grams water.

b) Estimated by GC using n-decane as internal standard.

c) Extraction work carried out at 400°C and 2000 psig.

TABLE X

Effect of temperature on extract yield in semi-continuous supercritical gas extraction of 300 grams Nova Scotia coal sample 1 with 5% tetralin in toluene at 1800 psig.

Temperature (°C)	cdl[b] (g)	Char (g)	% cdl (daf)	Material[a] Balance
375[c]	33.8	193.8	12.9	85.2
400	63.7	192.3	24.4	94.7
425	70.2	171.5	26.8	89.9

a) Includes 28 grams water.

b) Estimated by GC using n-decane as internal standard.

c) Wide fluctuation in temperature was observed reaching a maximum of 404°C and a minimum of 337°C.

TABLE XI

Effect of pressure on extract yield in semi-continuous supercritical gas extraction of 300 grams Nova Scotia coal sample 1 at 375°C.

Solvent	Pressure (psig)	cdl[b] (g)	Char (g)	% cdl (daf)	Material[a] Balance
5% Tetralin in Toluene	1800	33.8	193.8	12.9	85.2[c]
5% Tetralin in Toluene	2300	59.4	184.9	22.7	90.8
10% Tetralin in Toluene	1800	73.0	180.0	27.9	93.7
10% Tetralin in Toluene	2300	76.9	166.1	29.4	90.3

a) Includes 28 grams water.

b) Estimated by GC using n-decane as internal standard.

c) Wide fluctuation in temperature was observed reaching a maximum of 404°C and a minimum of 337°C.

TABLE XII

Char weights obtained in semi-continuous supercritical gas extraction of 300 grams of Nova Scotia coal under various experimental parameters.

Sample No.	Solvent	Solvent/ Coal Ratio(w/w)	Temp (°C)	Pressure (psig)	Char Weight (g)
2	Toluene	10.4	400	2000	214.6
2	Toluene	14.2	400	2000	208.3
2	3% Tetralin in Toluene	9.8	300-375	2000	228.5
1	Toluene	9.5	400	2000	204.9
1	Toluene	17.6	375	2300	195.9
1	5% Tetralin in Toluene	13.4	337-404	1800	193.8
1	5% Tetralin in Toluene	26.5	375	1800	196.1
1	5% Tetralin in Toluene	16.1	375	2300	184.9
1	5% Tetralin in Toluene	24.4	400	1800	192.3
1	5% Tetralin in Toluene	22.1	425	1800	171.5
1	5% Tetralin in Toluene	14.2	425	1800	202.2
1	10% Tetralin in Toluene	24.6	375	1800	180.0
1	10% Tetralin in Toluene	22.7	375	2300	166.1
1	10% Tetralin in Toluene	11.6	425	2300	208.2
1	Varsol	16.5	400	2000	212.4
1	Varsol	22.9	425	2300	211.5
1	35% Toluene in Varsol	21.3	425	2300	217.1
1	Varsol + Toluene + Tetralin (6:3:1)	21.1	375	2300	216.6
1	10% Tetralin in Varsol	22.7	415	2300	217.5

TABLE XIII

Continuous supercritical toluene extraction of Forestburg subbituminous coal and Nova Scotia coal sample 1 at 425°C and 3000 psig.

	COAL SAMPLES			
Extraction Data	Nova Scotia Bituminous	Forestburg Subbituminous	Forestburg Subbituminous	Forestburg Subbituminous
Coal Weight (g)	103.0	100.0	114.2	146.6
Solvent/Coal Ratio (W/W)	12.4	11.9	11.0	7.2
Pumping Rate (ml/min.)	14.5	15.7	13.5	11.8
Extraction Time (min.)	104.0	89.0	110.0	105.0
Residence Time (min.)	5.9	5.4	6.3	7.2
Water (g)	9.6	10.2	11.4	14.9
Cdl (g)	28.3	24.0	18.4	20.8
Char (g)	61.8	60.0	75.0	105.7
% cdl (daf)	31.5	29.3	19.6	17.3
Material Balance	96.8	94.2	91.8	96.5

TABLE XIV

Solvent analysis of cdl obtained by semi-continuous supercritical toluene extraction of Nova Scotia butiminous coal at 400°C and 2000 psig.

Sample	Solvent Soluble/Insoluble	Weight (g)	% of Total
1[a]	-----/THF (Insoluble)	0.30	3.1
	THF/Toluene (Preasphaltene)	1.06	10.8
	Toluene/Pentane (Asphaltene)	3.15	32.1
	Pentane/----- (Oil)	4.60	46.9
	% Recovery		92.9
2[b]	-----/THF (Insoluble)	0.44	4.3
	THF/Toluene (Preasphaltene)	1.01	9.9
	Toluene/Pentane (Asphaltene)	2.88	28.3
	Pentane/----- (Oil)	5.36	52.7
	% Recovery		95.2

a) 9.81 grams of solvent free cdl was used for the analysis.

b) 10.18 grams of solvent free cdl was used for the analysis.

TABLE XV

Separation of asphaltene into acid-neutral and basic fractions.

Sample[a)]	Fraction	Weight (g)	% of Total
1	Insoluble	0.13	5.2
	Acid-Neutral	0.91	36.1
	Basic	0.80	31.7
	% Recovery		73.0
2	Insoluble	0.22	7.6
	Acid-Neutral	1.17	40.6
	Basic	0.63	21.9
	% Recovery		70.1

a) 2.52 grams of asphaltene from coal sample 1 and 2.88 grams of asphaltene from coal sample 2 were used for the analysis.

TABLE XVI

Nmr spectral data for the cdl fractions obtained from the extraction of Nova Scotia bituminous coal (sample 2) with toluene at 400°C and 2000 psig.

Fraction	cdl (g)	Ha[a)]
1	9.0	0.27
2	11.4	0.37
3	8.4	0.42
4	7.7	0.46
5	5.7	0.42
6	2.0	0.43
7	1.8	0.41
8	2.9	0.41
9	2.0	0.43
10	1.3	0.43
11	1.5	0.43
12	2.3	0.37

a) Ratio of aromatic and phenolic hydrogen to total hydrogen.

TABLE XVII

Comparison of pmr data for fractions of cdl obtained by semi-continuous supercritical toluene extraction of Nova Scotia bituminous coal and Western Canada subbituminous coal.

Sample	Fraction	Ha[b]
Nova Scotia bituminous coal 1[a]	Preasphaltene	0.43
	Basic asphaltene	0.36
	Acid/Neutral asphaltene	0.42
	Oil	0.26
Nova Scotia bituminous coal 2	Preasphaltene	0.35
	Basic asphaltene	0.42
	Acid/Neutral asphaltene	0.38
	Oil	0.32
Western Canadian subbituminous coal	Preasphaltene	0.32
	Basic asphaltene	0.37
	Acid/Neutral asphaltene	0.32
	Oil	0.25

a) Metallurgical coal.

b) Ha is the ratio of aromatic and phenolic hydrogen to total hydrogen.

TABLE XVIII

Band assignments for the FT-IR spectrum of oil obtained from the supercritical toluene extraction of Nova Scotia coal sample 2.

Wave Number cm^{-1}	Assignment
3525] 3380]	Hydrogen bonded phenolic OH or NH stretching
3015	Aromatic C-H
2945] 2915] 2842]	Aliphatic CH, CH_2 and CH_3
1600] 1490]	Aromatic ring stretching
1447	CH_2 and CH_3 bending
1375	CH_3 groups
1255] 1190] 1150] 1080] 1027]	C-O stretch and O-H bending phenoxy structures, ethers
870] 807] 747] 700]	Aromatic C-H out of plan vibrational modes

TABLE XIX

Proximate analysis and calorific value of chars obtained from semi-continuous supercritical toluene extraction of two samples of Nova Scotia high volatile bituminous coal at 400°C and 2000 psig.

Sample[a)]	Ash	Volatile Matter	Fixed Carbon	Btu/lb
Char from coal 1	4.3	17.3	78.4	14654
Char from coal 2	4.6	15.8	79.6	14301
Coal 1	3.2	34.7	62.1	14928
Coal 2	3.8	34.5	61.7	14147

a) Dry basis.

TABLE XX

Ultimate analysis of chars obtained from semi-continuous supercritical toluene extraction of two samples of Nova Scotia high volatile bituminous coal at 400°C and 2000 psig.

Sample	Determined	C	H	N	S	O	H/C
Char from coal 1	Dry basis	84.97	3.79	1.61	1.06	4.24	
	daf	88.82	3.96	1.68	1.11	4.43	0.54
Char from coal 2	Dry basis	83.98	3.79	1.49	1.84	4.26	
	daf	88.07	3.97	1.56	1.93	4.47	0.54
Coal 1	Dry basis	82.93	5.40	1.69	1.25	5.49	
	daf	85.70	5.58	1.74	1.29	5.67	0.78
Coal 2	Dry basis	79.10	5.05	1.45	2.36	8.29	
	daf	82.18	5.25	1.51	2.46	8.61	0.77

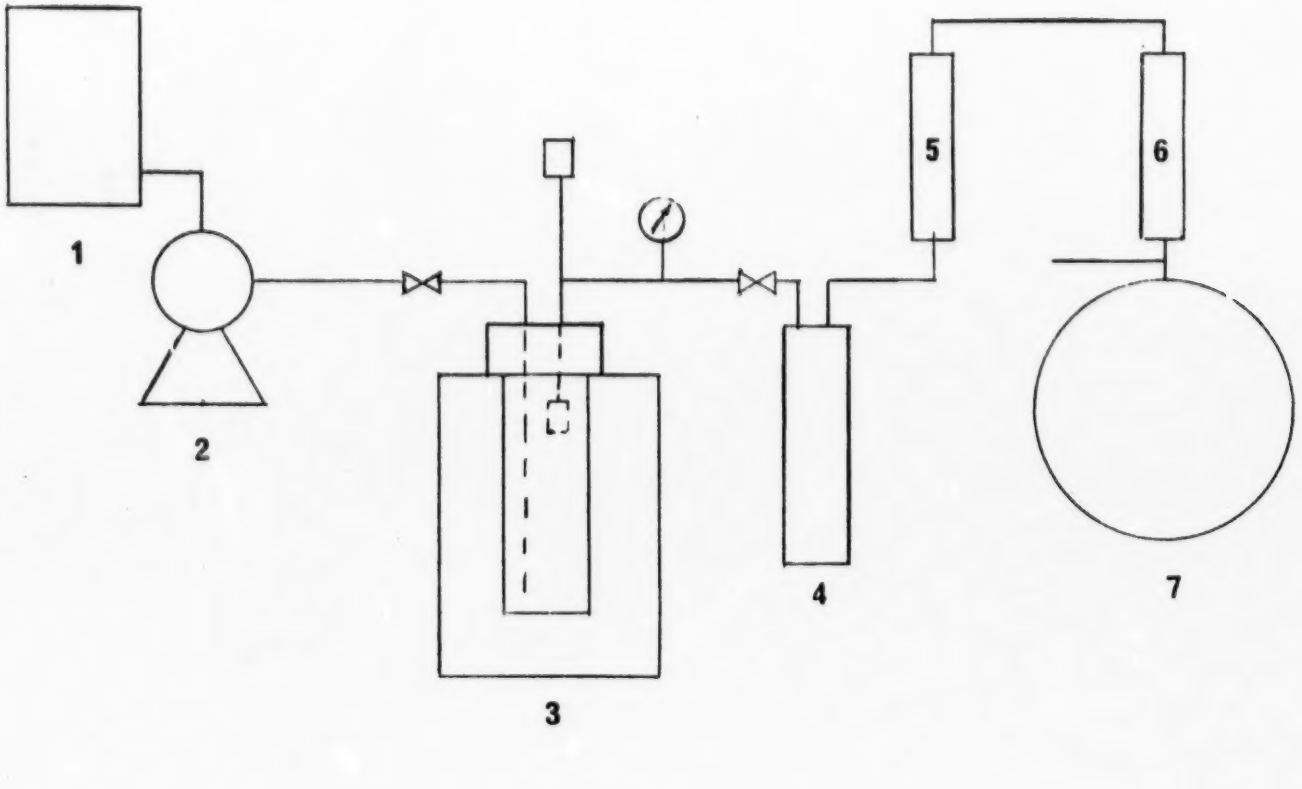

Figure 1: Equipment flow for supercritical gas extraction of coal.
1. Solvent reservoir; 2. Pump; 3. Autoclave and heater; 4. Catch pot ;
5. Demister; 6. Condenser; 7. Recovered solvent.

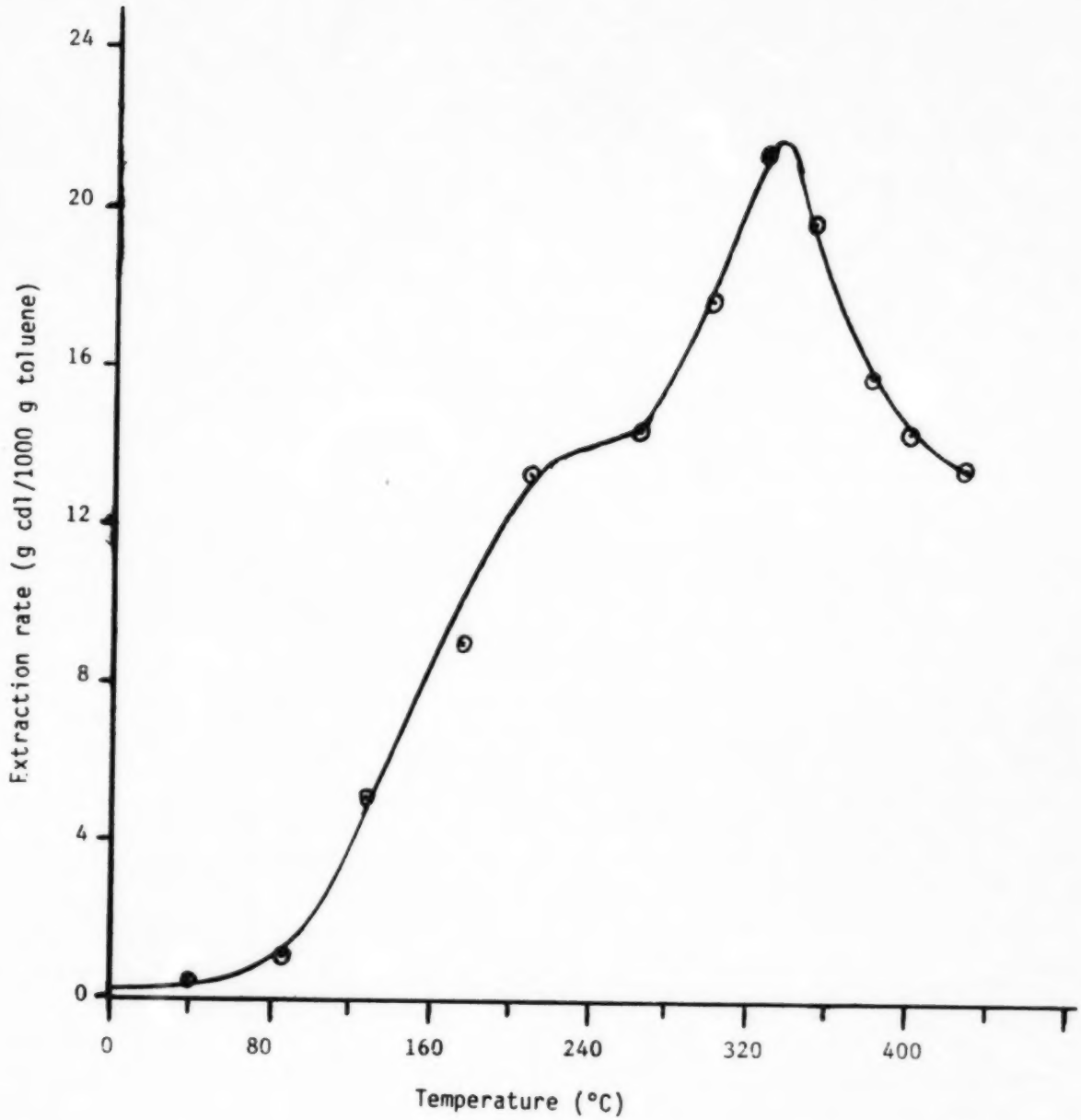

Figure 2: Plot of cdl extraction rate as a function of temperature for toluene extraction of Nova Scotia bituminous coal sample 2.

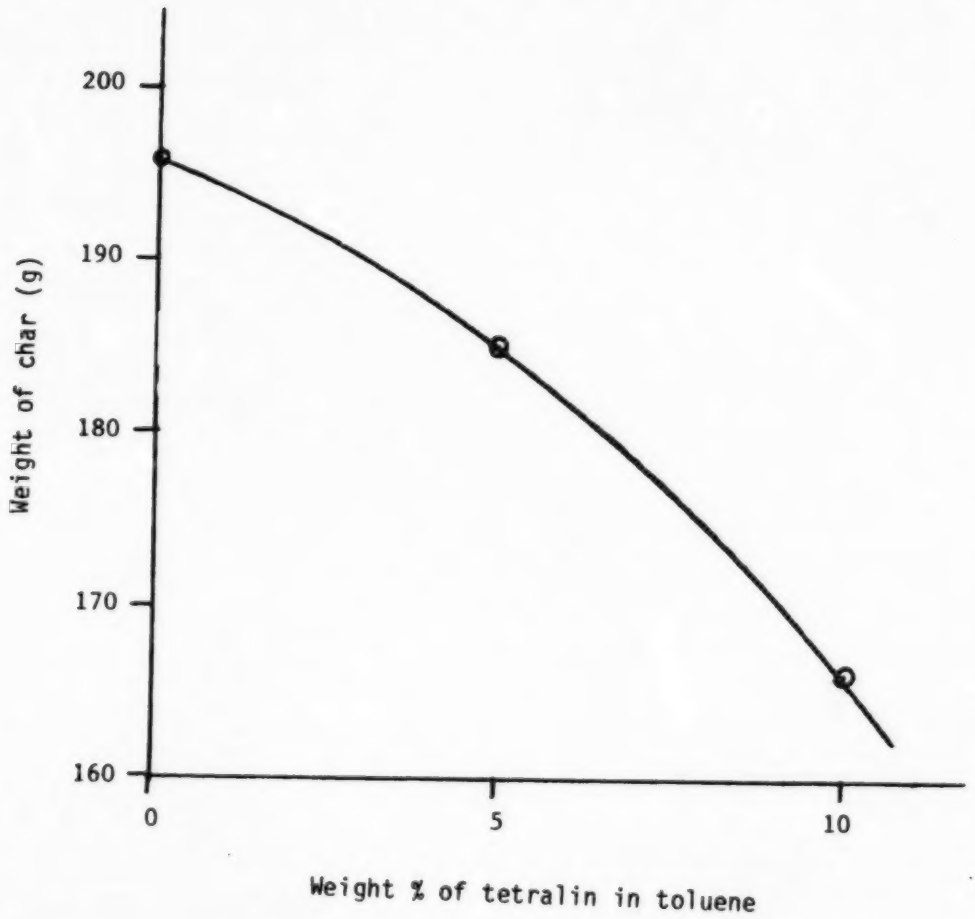

Figure 3: Effect of weight percent of tetralin in toluene on the amount of char obtained in the supercritical gas extraction of 300 grams of Nova Scotia coal sample 1 at 375°C and 2300 psig.

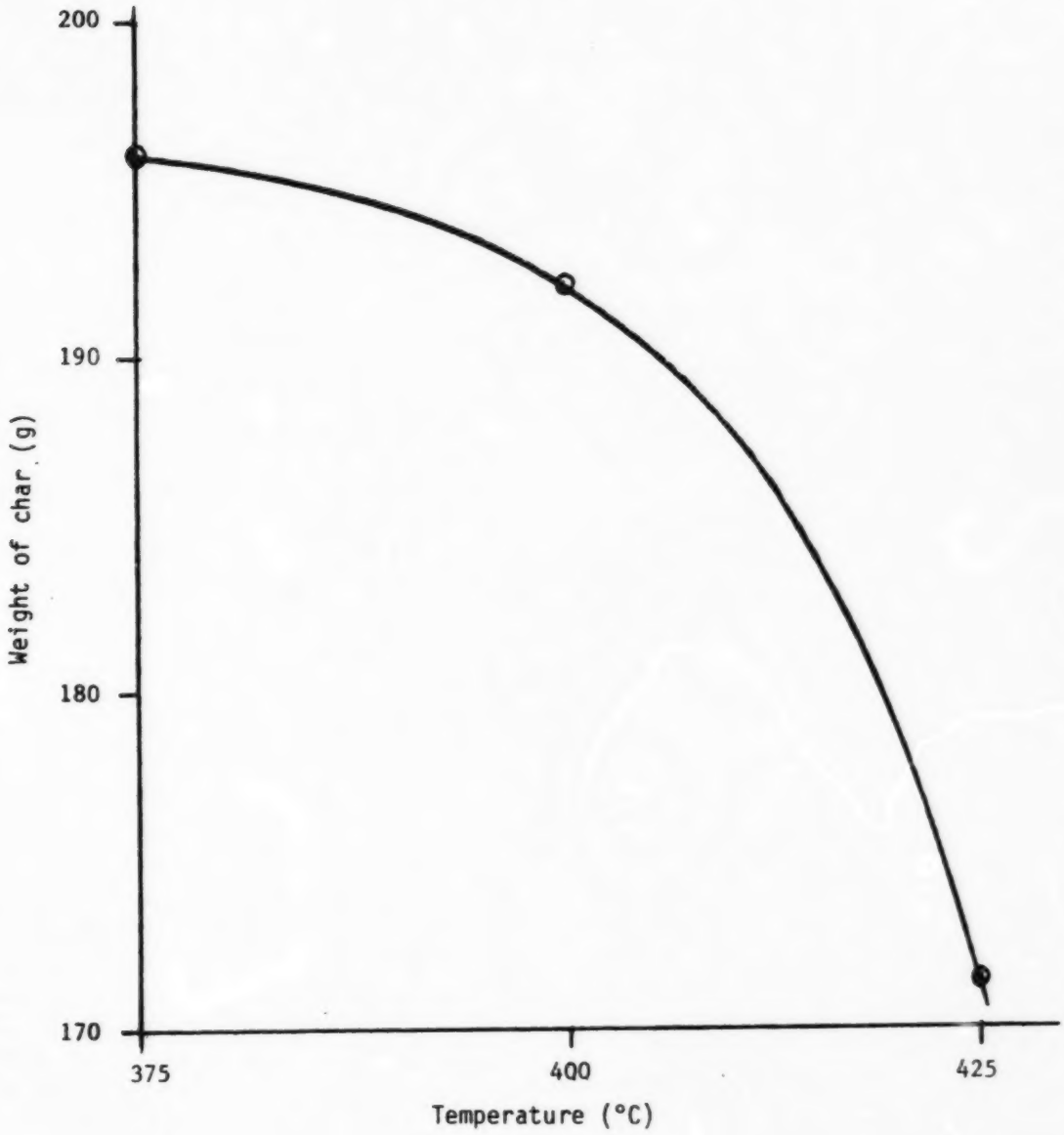

Figure 4: Effect of temperature on the amount of char obtained in the supercritical gas extraction of 300 grams of Nova Scotia coal sample 1 with 5% tetralin in toluene at 1800 psig.

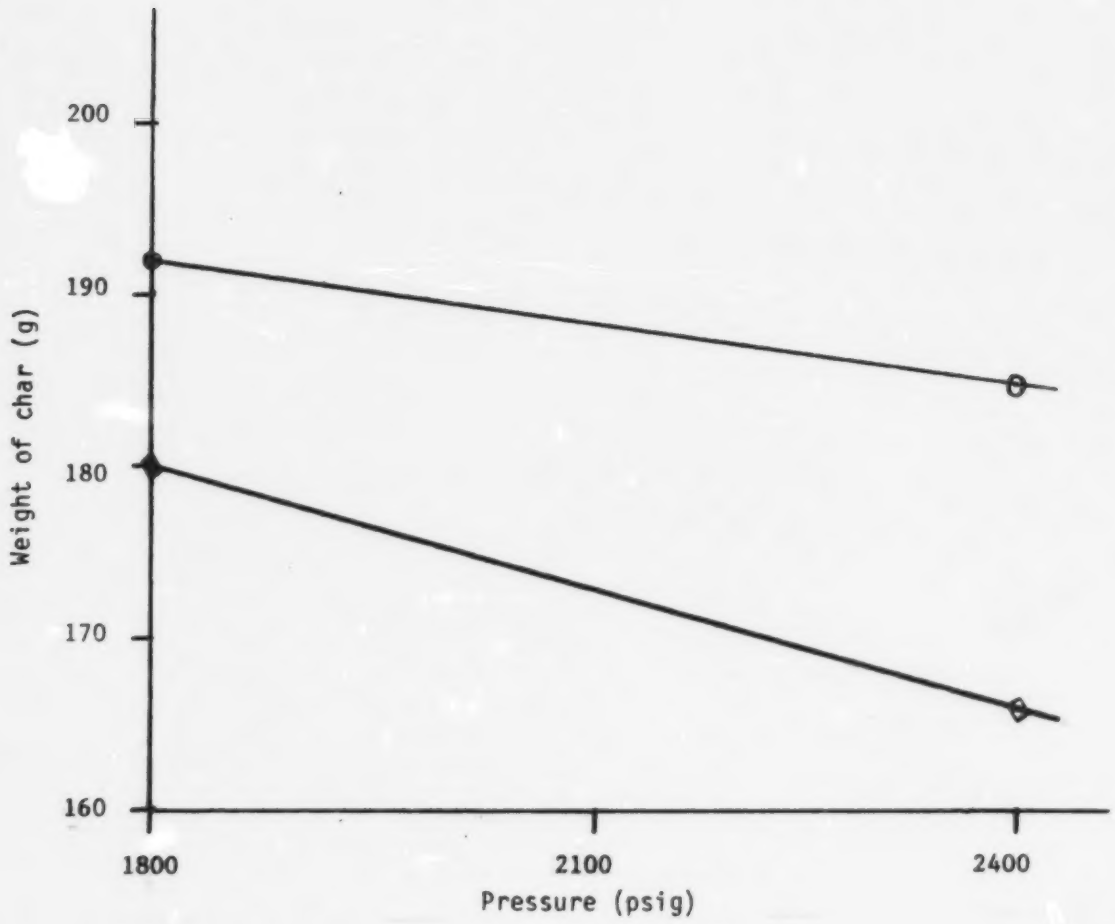

Figure 5: Effect of pressure on the amount of char obtained in the supercritical gas extraction of 300 grams of Nova Scotia coal sample 1 at 375°C.
⊙: Extraction carried out with 5% tetralin in toluene.
◈: Extraction carried out with 10% tetralin in toluene.

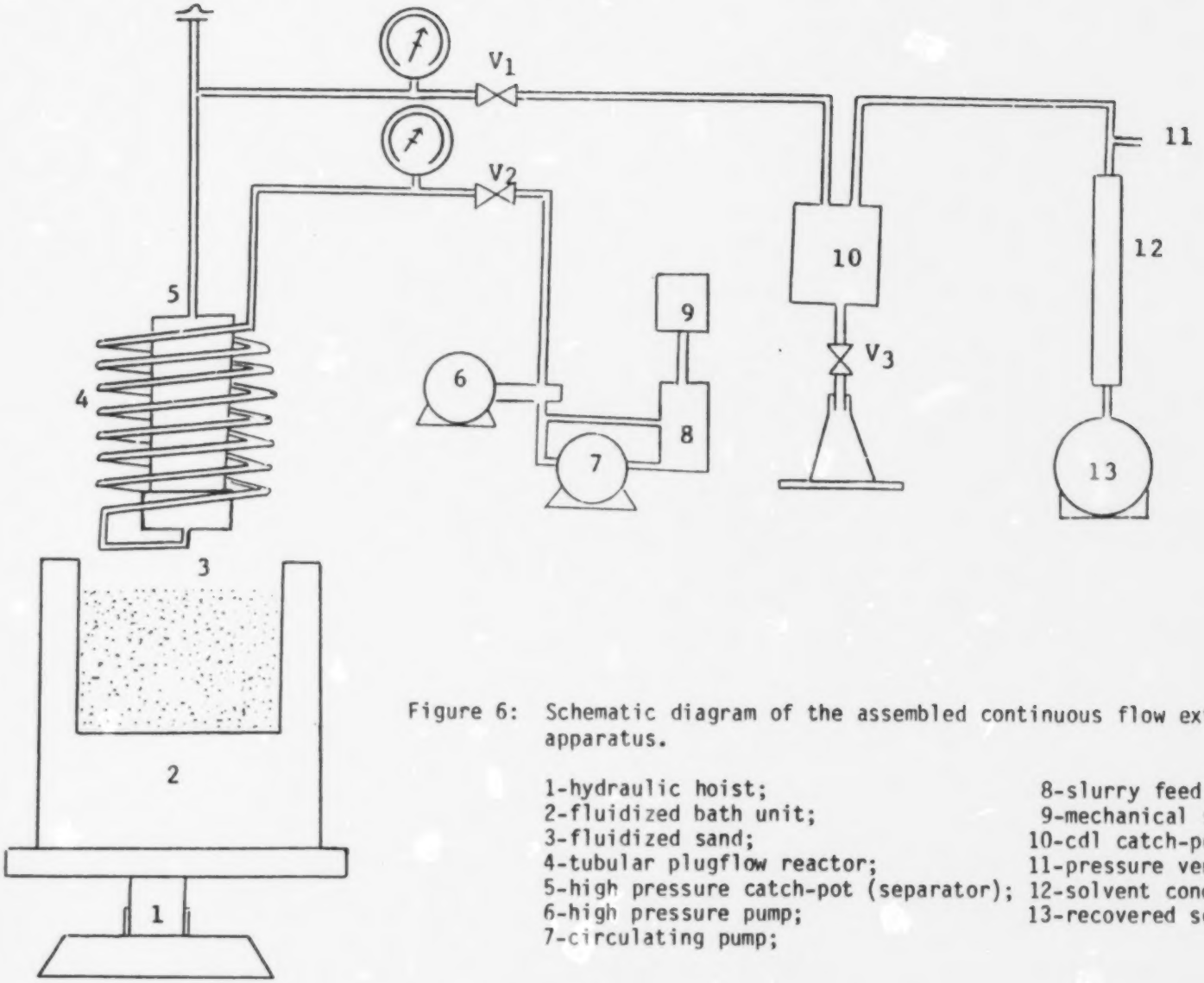

Figure 6: Schematic diagram of the assembled continuous flow extraction apparatus.

1-hydraulic hoist;
2-fluidized bath unit;
3-fluidized sand;
4-tubular plugflow reactor;
5-high pressure catch-pot (separator);
6-high pressure pump;
7-circulating pump;
8-slurry feed vessel;
9-mechanical stirrer;
10-cdl catch-pot;
11-pressure vent;
12-solvent condenser;
13-recovered solvent receiver.

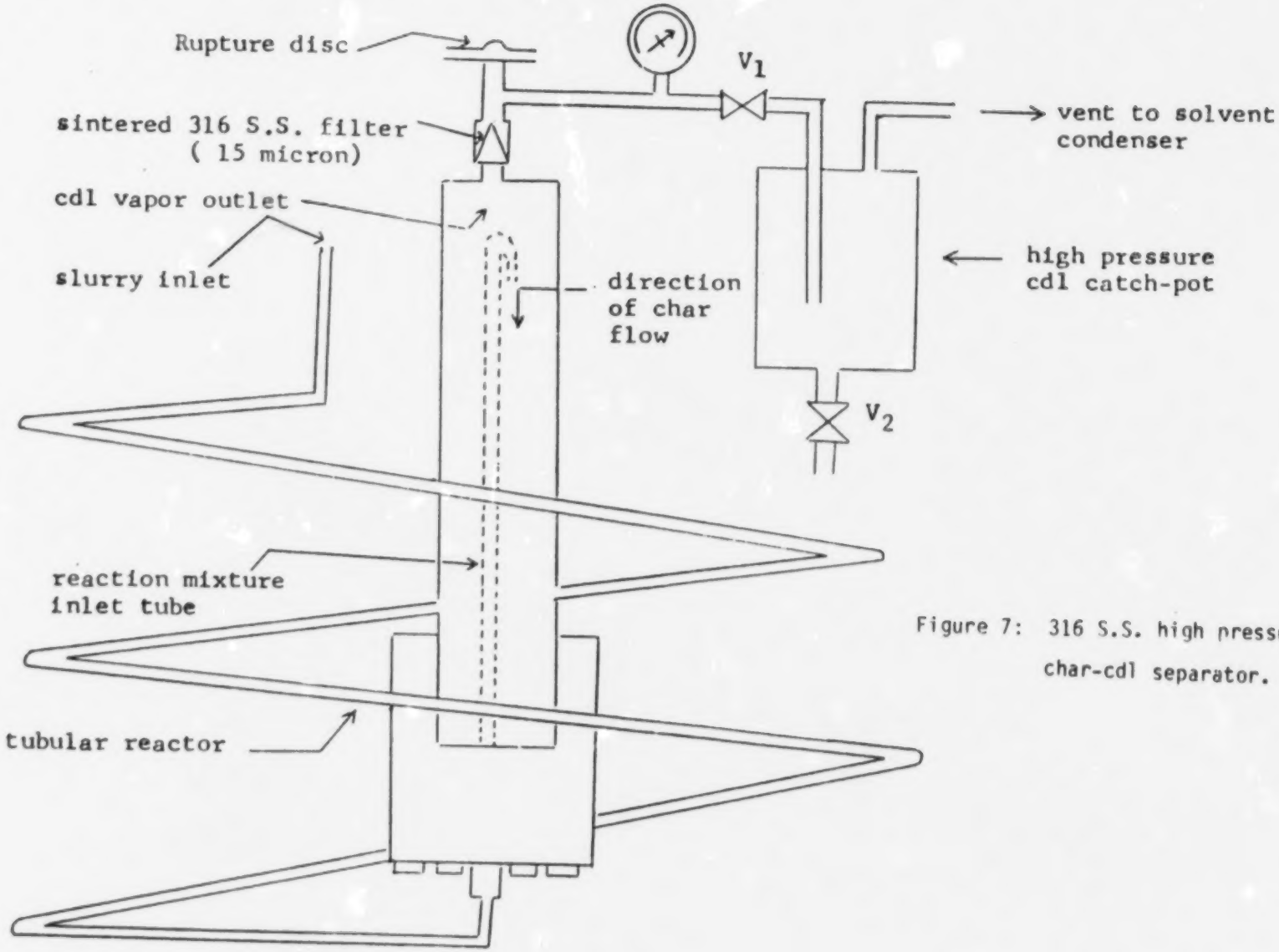

Figure 7: 316 S.S. high pressure char-cdl separator.

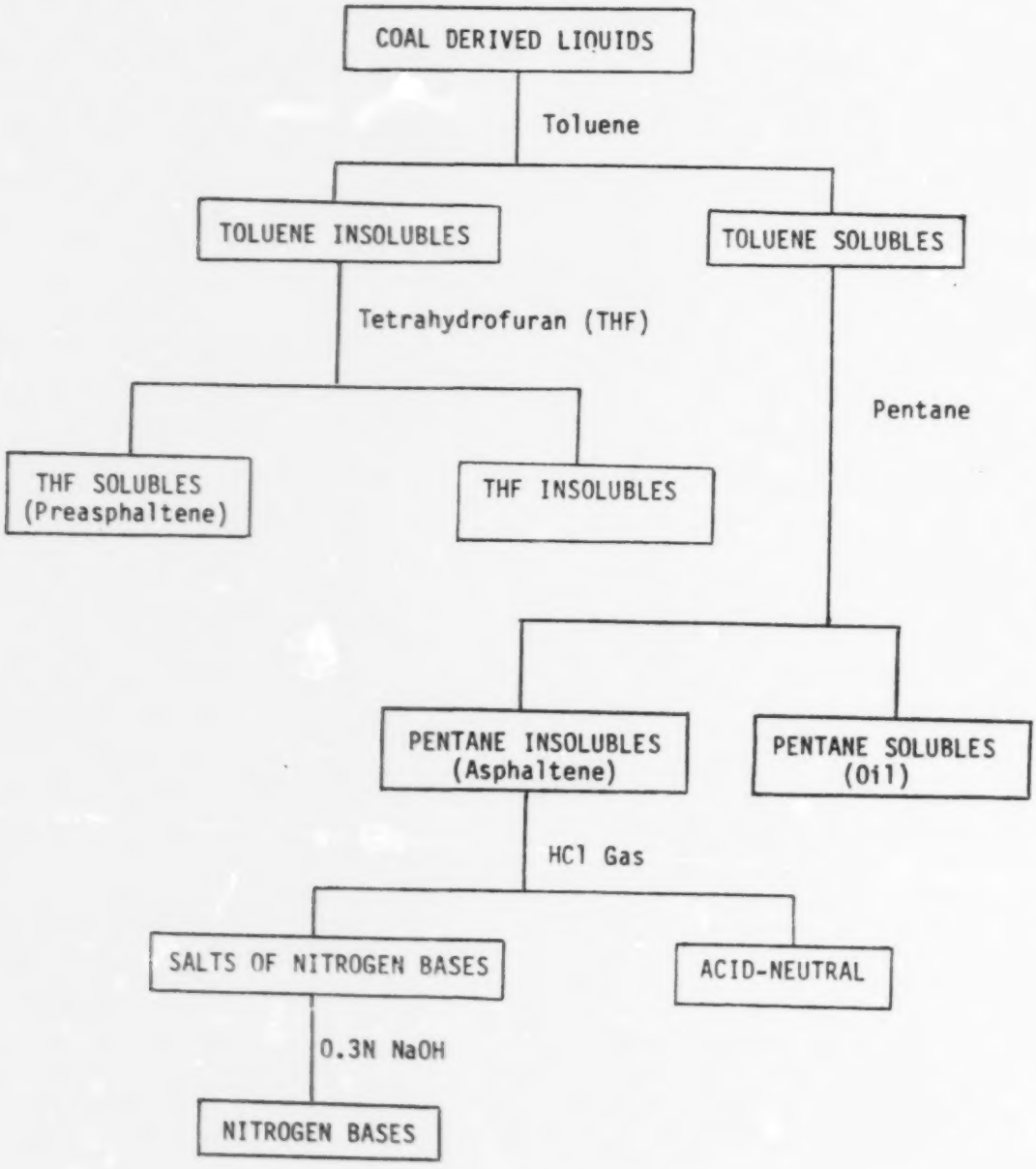

Figure 8: Flow chart for solvent analysis of coal derived liquids (cdl).

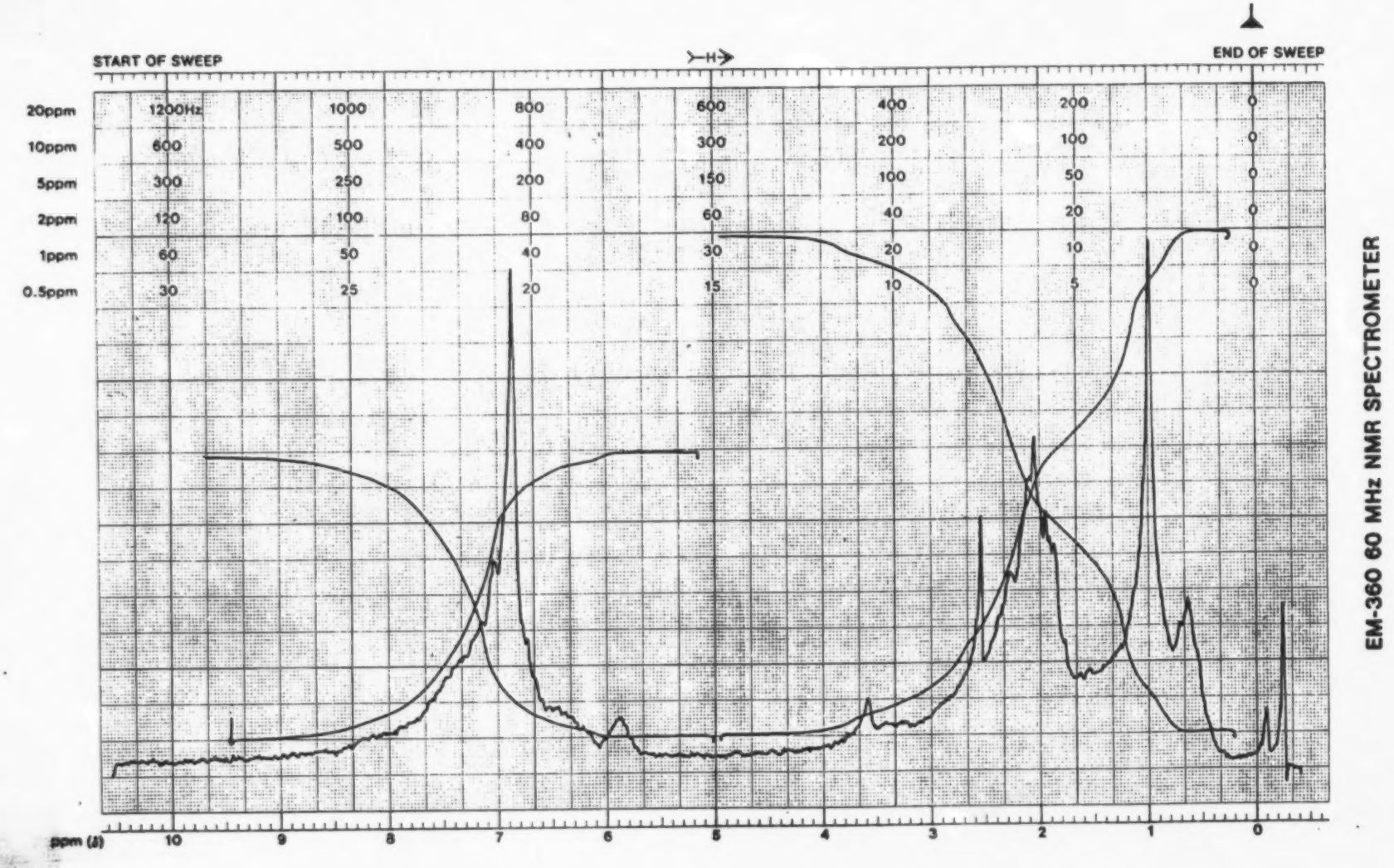

Figure 9: The pmr spectrum ($CDCl_3$) of oil obtained by solvent separation of cdl which were obtained from Nova Scotia coal sample 2 by supercritical toluene extraction at 400° and 2000 psig.

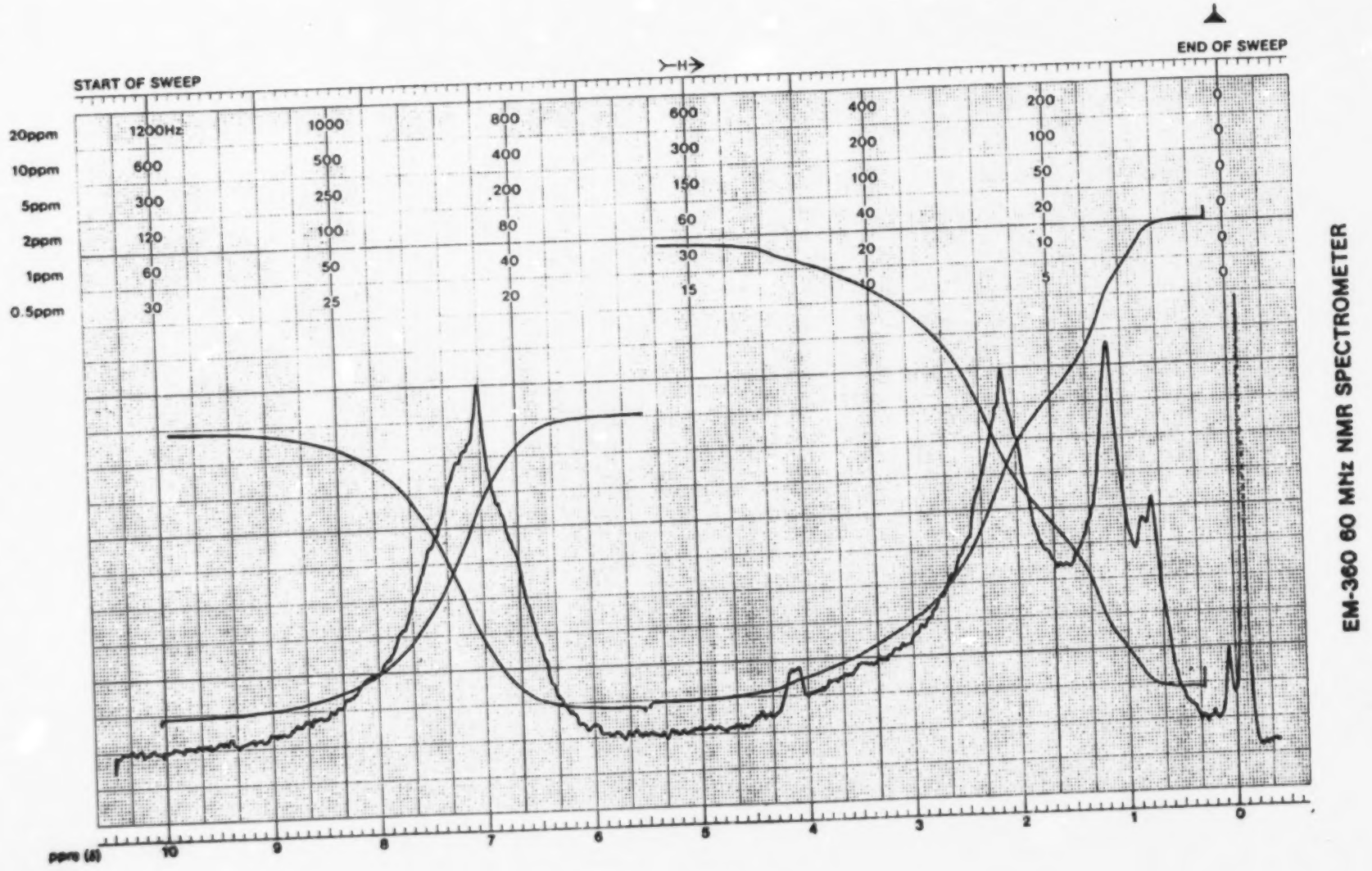

Figure 10: The pmr spectrum ($CDCl_3$) of the acid/neutral fraction of asphaltene obtained by solvent separation of cdl. The cdl were obtained by supercritical toluene extraction of Nova Scotia coal sample 2 at 400°C and 2000 psig.

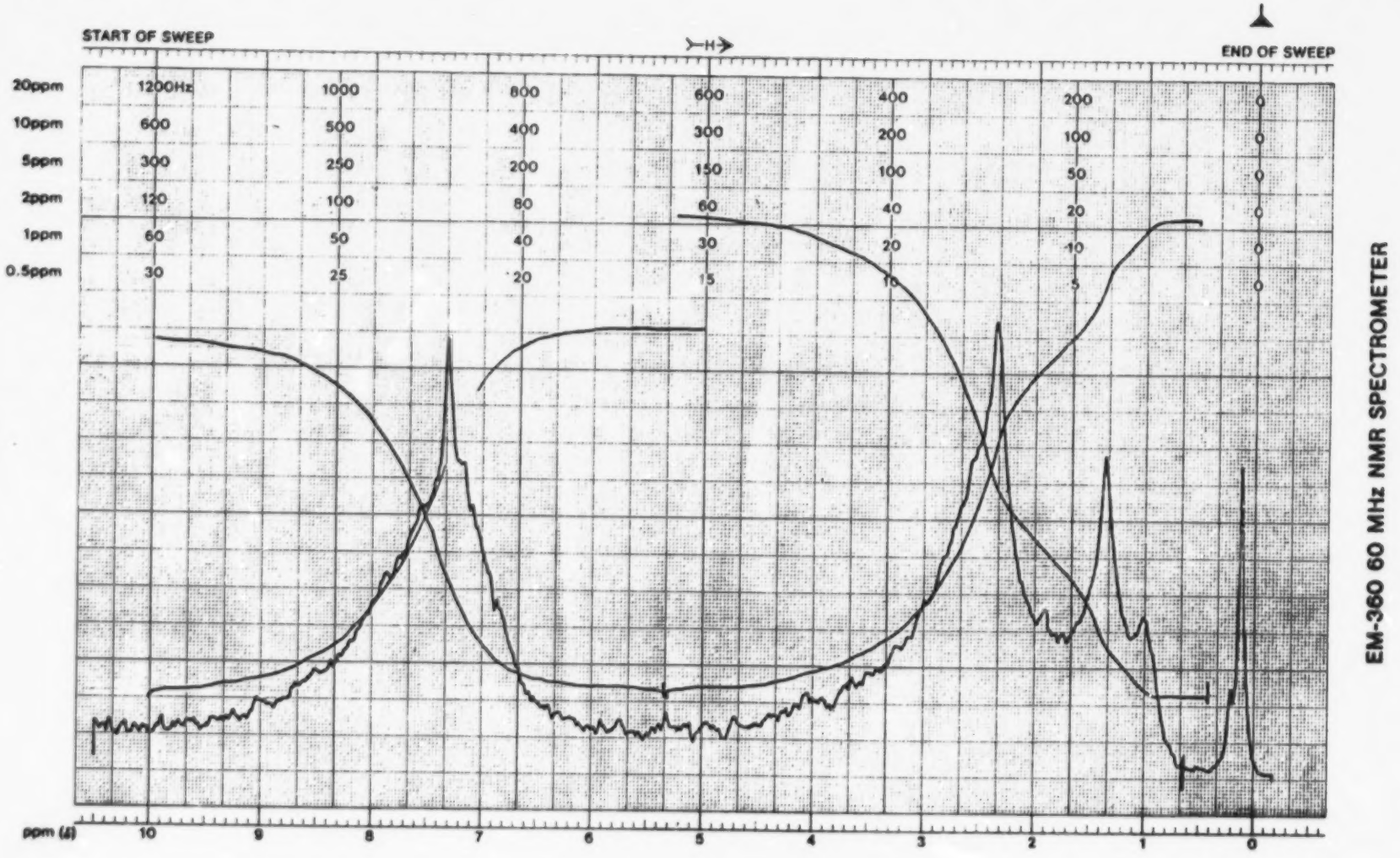

Figure 11: The pmr spectrum ($CDCl_3$) of the basic fraction of asphaltene obtained by solvent separation of cdl. The cdl were obtained by supercritical toluene extraction of Nova Scotia coal sample 2 at 400°C and 2000 psig.

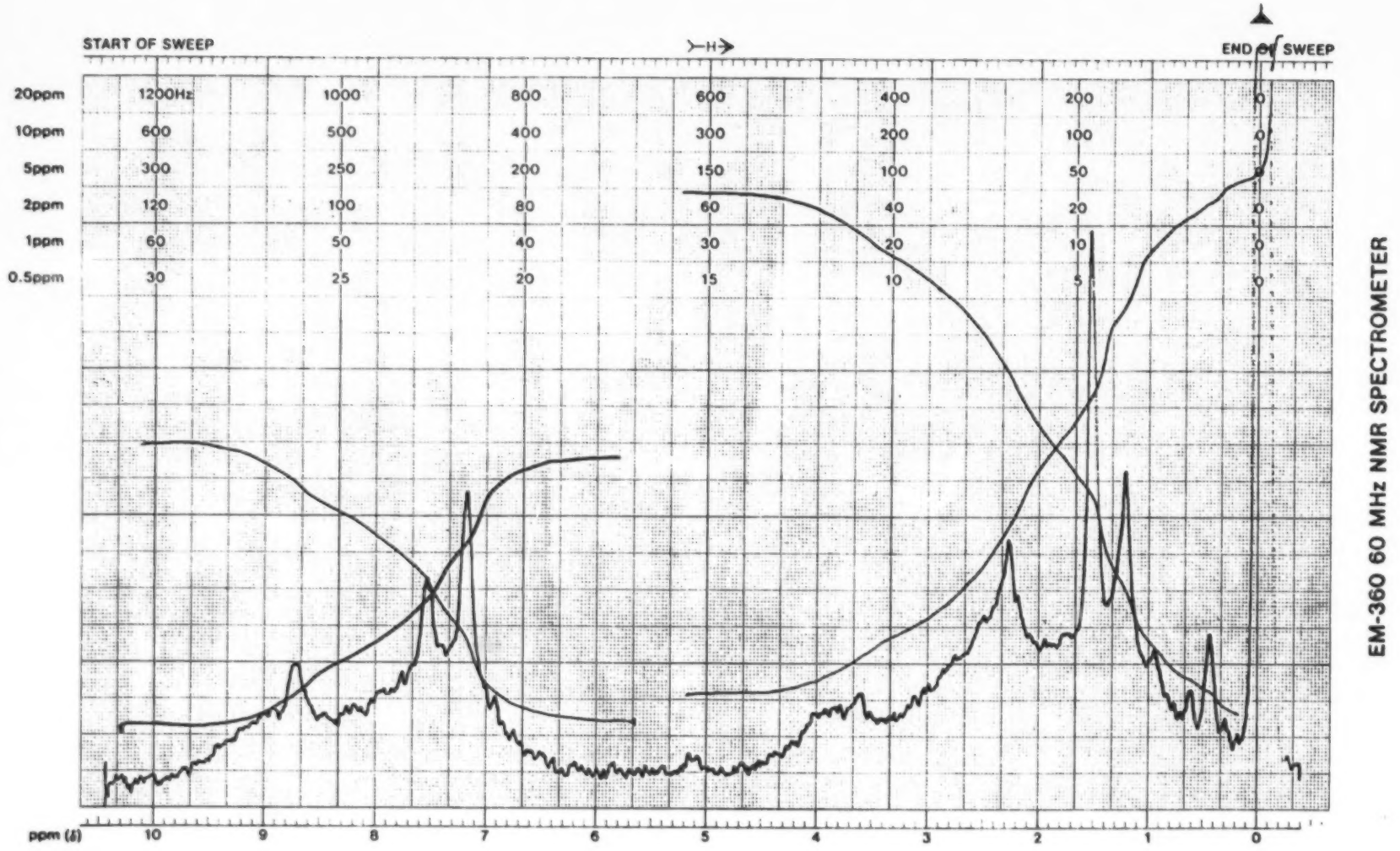

Figure 12: The pmr spectrum (pyridine -d_5) of preasphaltene obtained by solvent separation of cdl. The cdl were obtained by supercritical toluene extraction of Nova Scotia coal sample 2 at 400°C and 2000 psig.

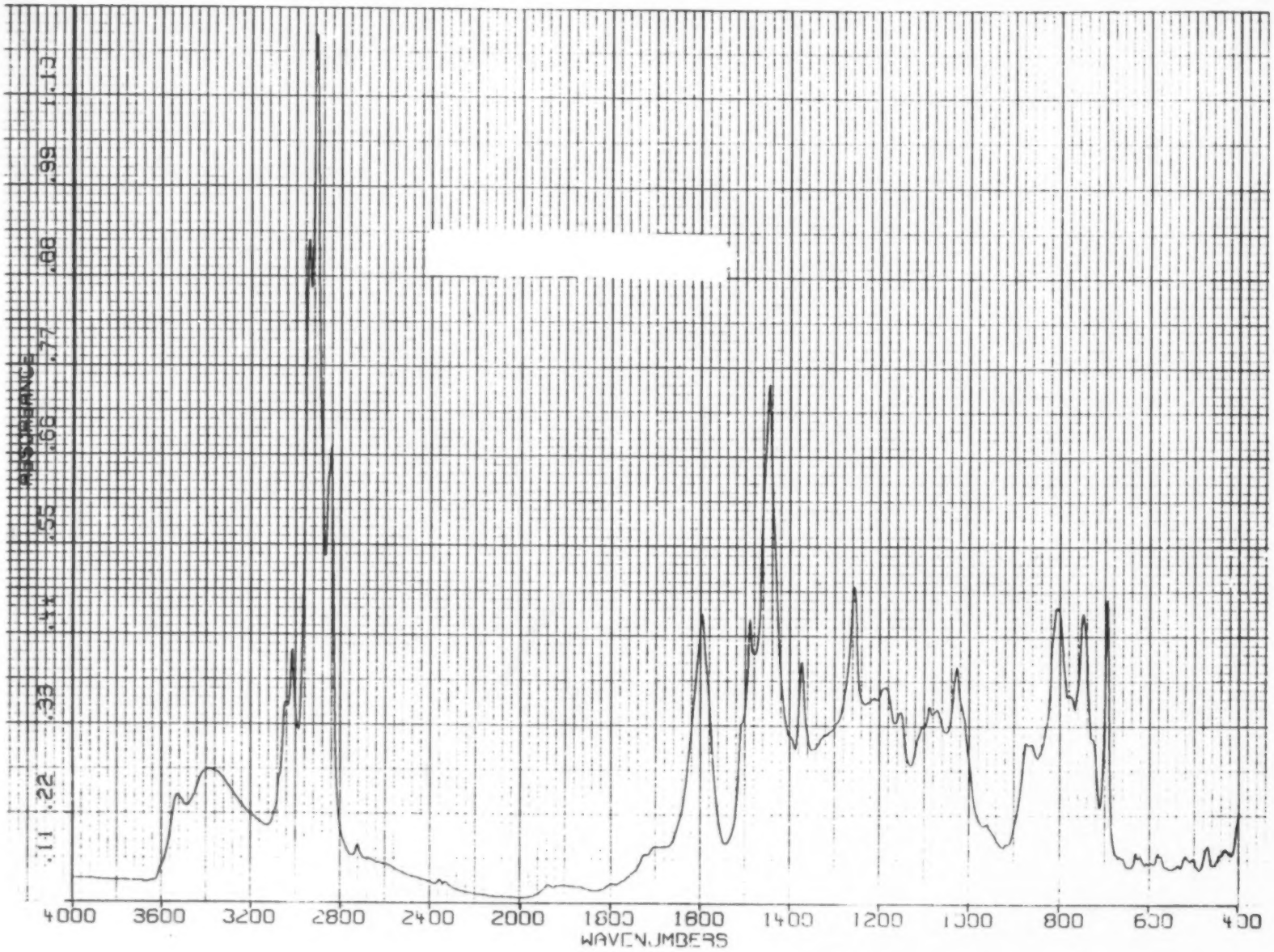

Figure 13: FT-IR spectrum (THF cast) of oil isolated by solvent separation of cdl obtained from Nova Scotia coal sample 2 by supercritical toluene extraction at 400°C and 2000 psig.

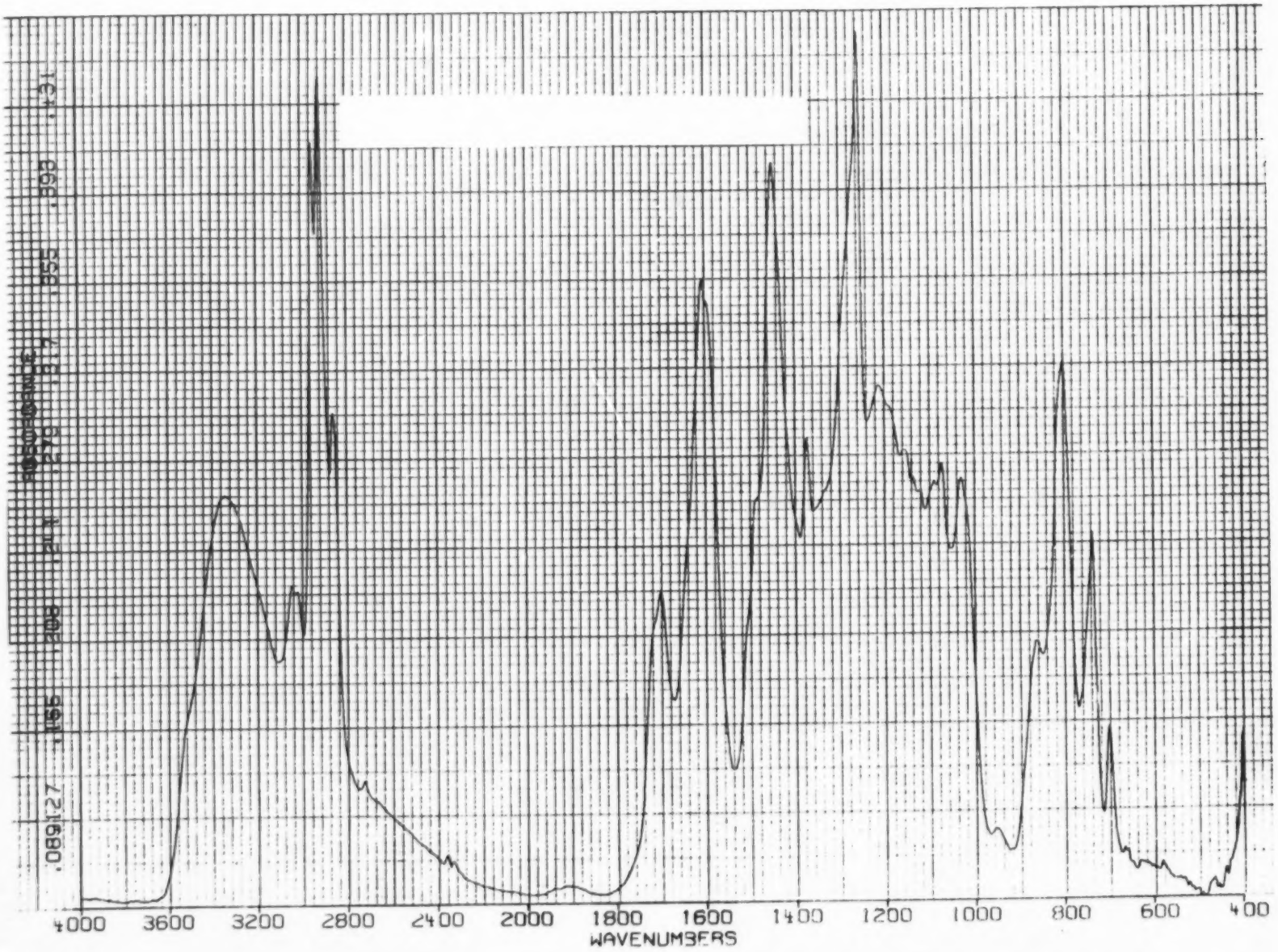

Figure 14: FT-IR spectrum (THF cast) of the acidic/neutral fraction of asphaltene isolated by solvent separation of cdl obtained by supercritical toluene extraction of Nova Scotia coal sample 2 at 400°C and 2000 psig.

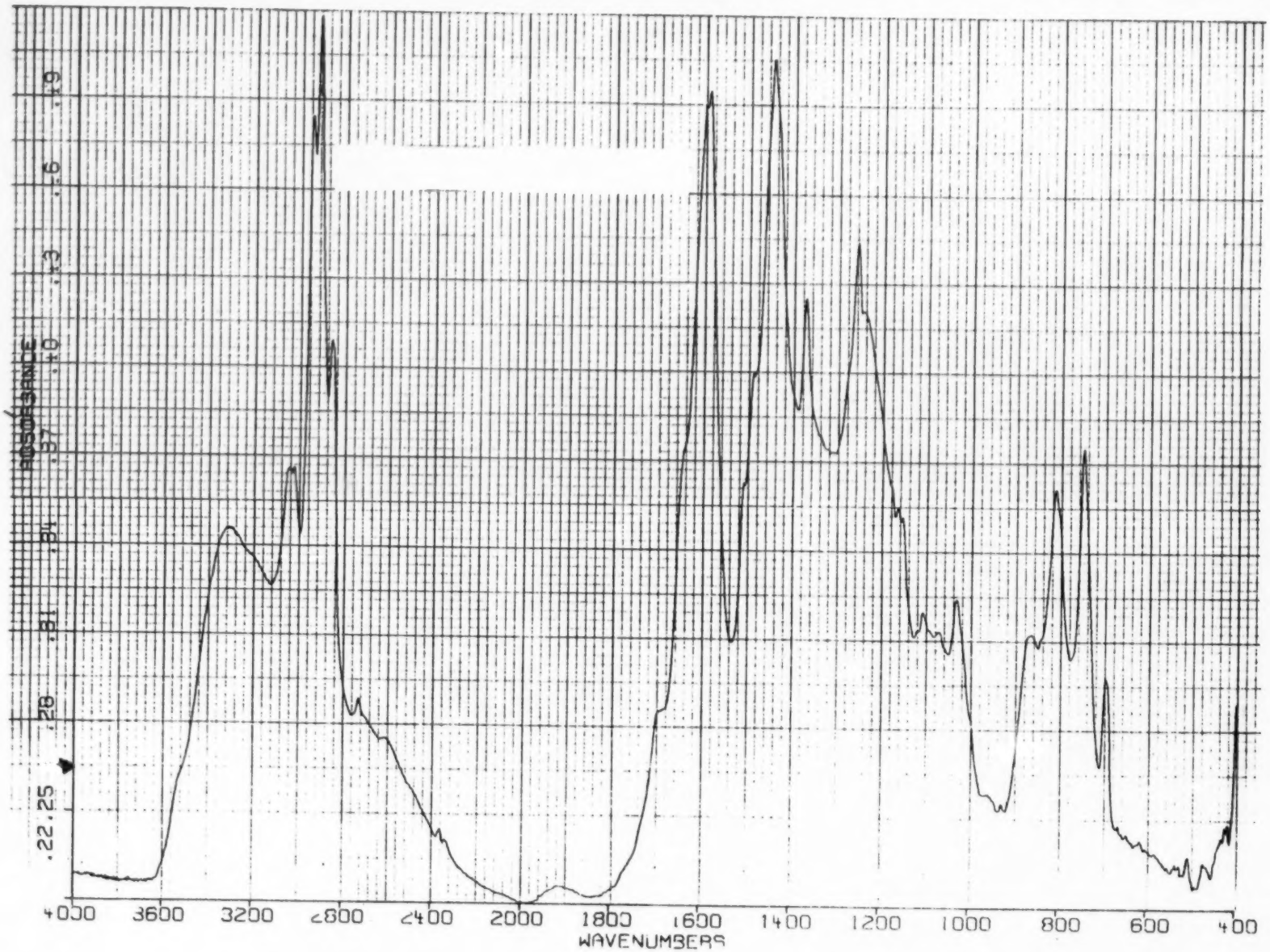

Figure 15: FT-IR spectrum (THF cast) of the basic fraction of asphaltene isolated by solvent separation of cdl obtained from Nova Scotia coal sample 2 by supercritical toluene extraction at 400°C and 2000 psig.

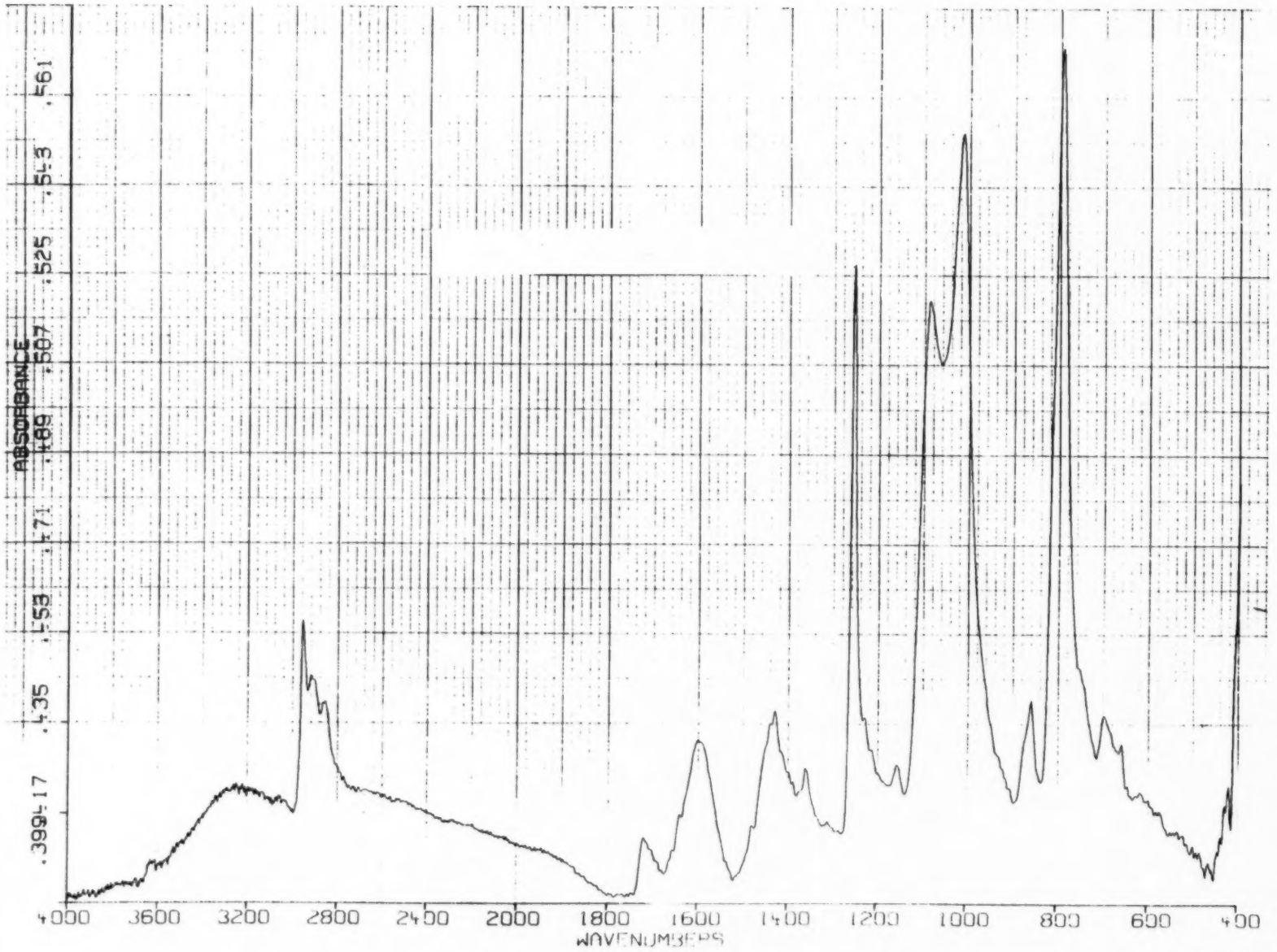

Figure 16: FT-IR spectrum (THF cast) of preasphaltene isolated by solvent separation of cdl obtained from Nova Scotia coal sample 2 by supercritical toluene extraction at 400°C and 2000 psig.

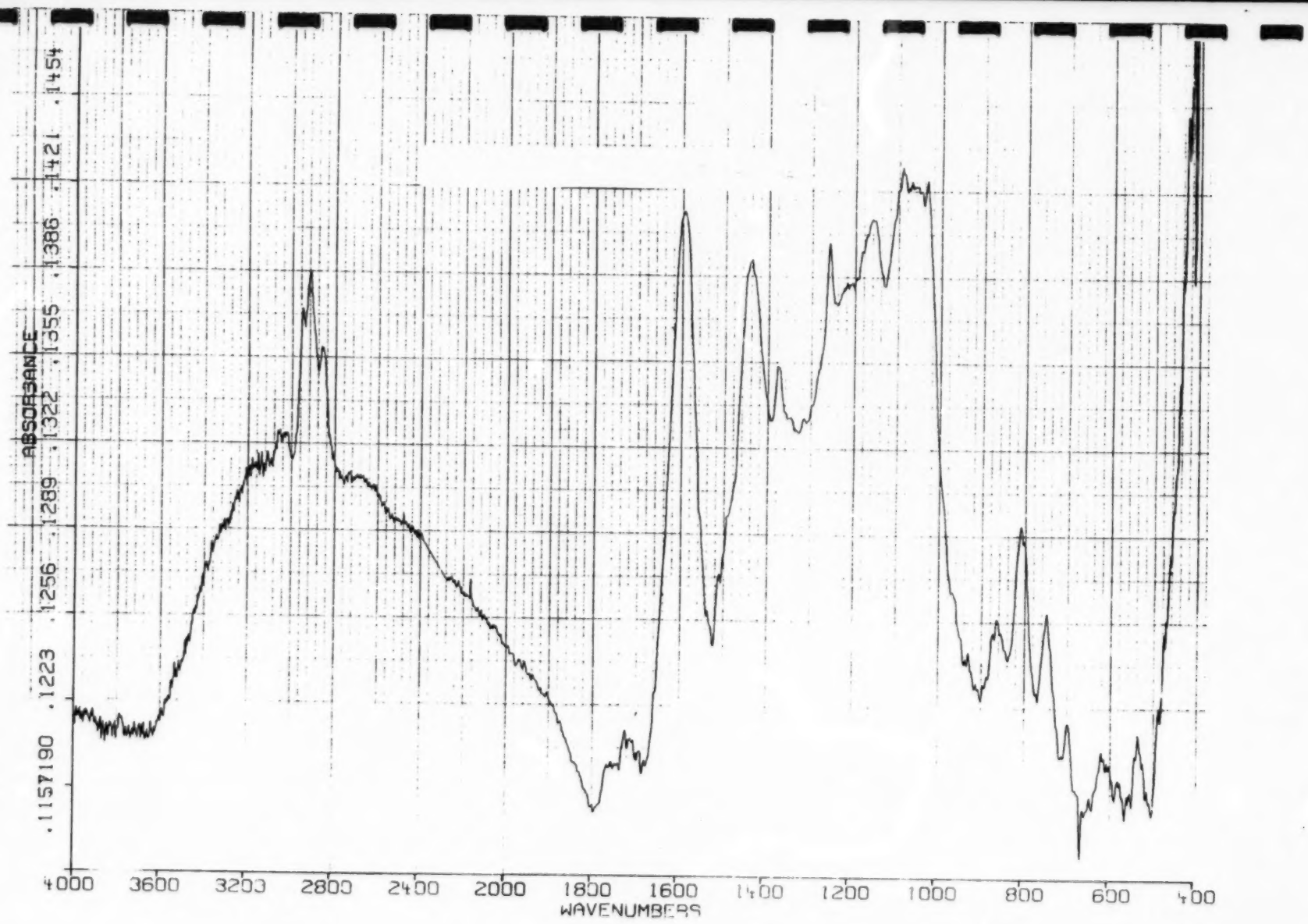

Figure 17: FT-IR spectrum (KBr disc) of THF insoluble material isolated by solvent extraction of cdl obtained from Nova Scotia coal sample 2 by supercritical toluene extraction at 400°C and 2000 psig.

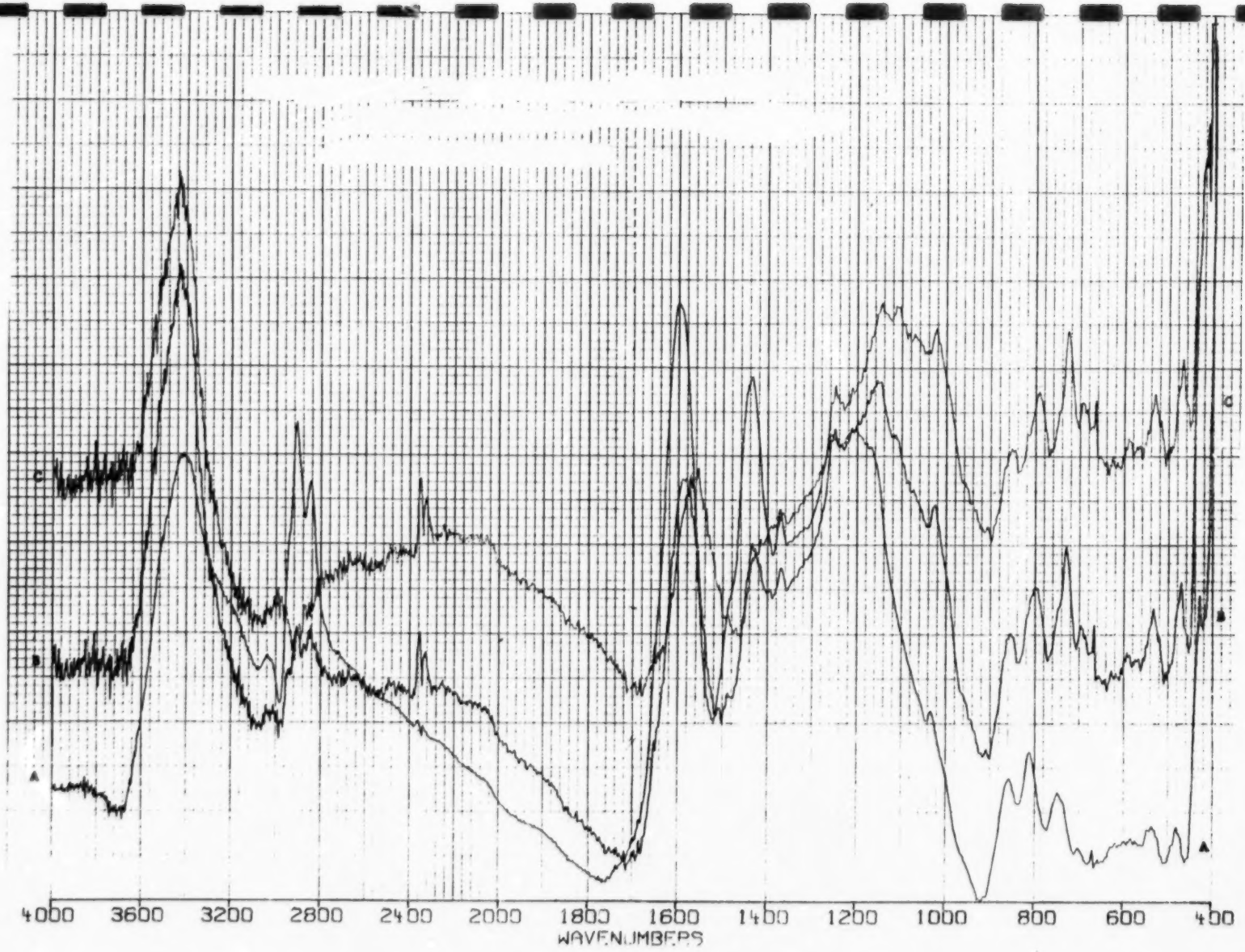

Figure 18: FT-IR spectra (KBr disc) of: A-Nova Scotia coal sample 2; B-char remaining after supercritical toluene extraction at 400°C and 2000 psig of the above coal; C-difference spectrum (B-A).

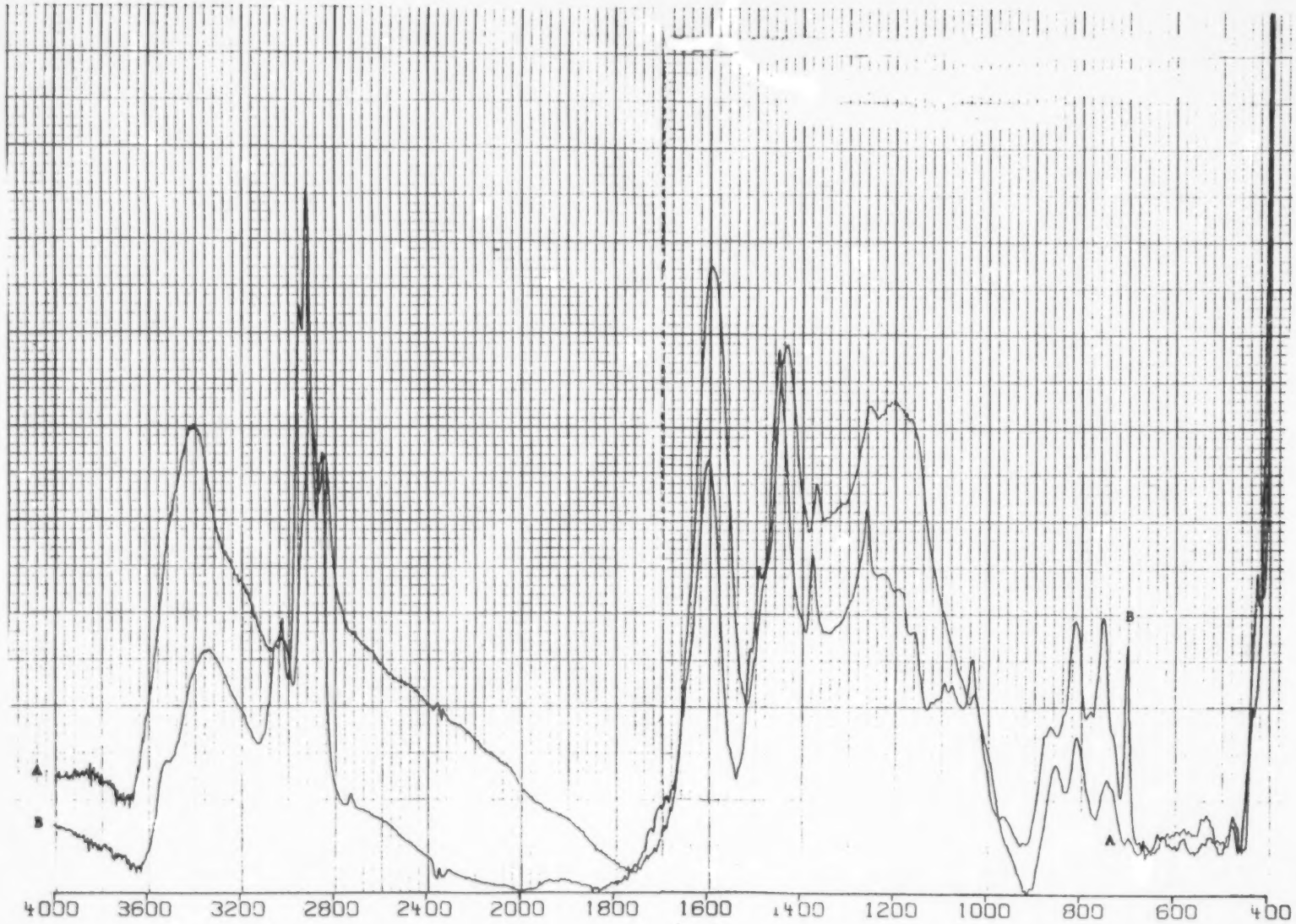

Figure 19: A-FT-IR spectrum (KBr disc) of Nova Scotia coal sample 2: B-FT-IR spectrum (THF cast) of cdl obtained from this coal by supercritical toluene extraction at 400°C and 2000 psig.